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The Effect of Growth Conditions on the Dye Absorption of Cotton Fibers

By W. M. MEBANE and A. A. O'KELLY

A Contribution from the Laboratories of the Tennessee State Teachers College at Murfreesboro

THE classification of cotton fibers according to growth conditions was first studied by Crum[1] who pointed out that the condition of the fibers represented the age of the cotton plant. Mitchel and Prideaux[2] classified cotton fibers as green, mature, and dead. Herzog[3] described dead fibers and added unripe fibers to his classification. Haller[4] described the properties of dead and green fibers. Sanford[5] reported that dead and undeveloped cotton are more reactive to nitration than normal cotton. The structure of cotton fibers has been described in detail by Bowman,[6] by Denham,[7] and by Balls[8].

Several different types of fibers have been noted. Certain fibers were called dead because something had interfered to halt the development of the fiber before the secondary filling with the successive growth rings of cellulose had been accomplished. This particular fiber seems to be only an empty cuticle. Other very small fibers which seemed to have no lumen were designated as green because they appeared to have been halted in growth before normal size had been obtained. The full sized which did not have the usual twist, but only a few convolutions, were supposed to contain an excess of cellulose which failed to contract normally upon drying.

An investigation of the relation between the growth condition of cotton fibers and the type of fiber developed was made by Mebane and Vilbrandt.[9]

In this study samples were taken during the growing season, and examined under the microscope for the types of fibers which were developed at various periods of growth. Samples taken when the boll was just opening showed a high content of fibers which showed lack of twist development, and also a high content of green fibers. Samples taken when the cotton was fully opened and standing out firmly from the boll showed a high percentage of normal fibers. Cotton which had ripened to the extent that it was falling from the boll showed a high percentage of fibers which exhibited signs of disintegration. These fibers were apt to be large in relative size, marked in the lumen, and to show considerable spottiness. Cotton which was collected after frost showed a high content of dead fibers, and also a high percentage of the green and undeveloped type. These fibers were classified as green, under-ripe, normal, and dead. It was assumed that since cotton is the fruit of a growing plant it should be expected to exhibit the same differences in growth development as other fruits. Although the names given to these various types of fibers may be of no particular significance, they are an accurate index to the growth condition of the fiber, and will be used in this paper to indicate the type of fiber and its growth condition.

Mebane and Vilbrandt[10] also pointed out that the quality of cotton might be improved by a more carefully supervised picking, and that in various samples of commercially dyed fabrics the percentage of actually dyed fibers varied from five per cent to ninety per cent, with the different classes of fibers affected differently by the various colors which had been applied.

It has been known for some time that various reagents, treatments, and the presence of certain impurities have strongly affected the dyeing properties of cotton. Knecht[11] observed that mercerization increases the affinity for direct dyes. Everest and Hall[12] observed that oxidized cotton showed a marked increase in affinity for dyes. Knecht

[1]J. Chem. Soc. 10, 44, (1863).
[2]"Fibers Used in Textile and Allied Industries".
[3]Chem. Ztg. 38, 1089-91. 1907-1100 (1914).
[4]Chem. Ztg. 32, 838.
[5]"Nitro Explosives" Crosby Lockwood and Son.
[6]"The Structure of the Cotton Fiber".
[7]Jour. Text. Inst., 1922, xiii. 99; 1923, xiv, 86.
[8]"The Development and Properties of Raw Cotton".
[9]Am. Dyestuffs Rep. XV, 1, 1926

[10]Loc. cit.
[11]Jour. Soc. Dyers & Col., 1908 xxiv. 67 and 107.
[12]Jour. Soc. Dyers & Col. 1921, xxxvii 229.

TABLE I

Table indicating manner of dyeing cotton fibers.

Sample Number	*Type of cloth*	*Type of Dyeing*	*Procedure*	
1	Bleached	Direct	10 Minutes at 95°C.	
2	Unbleached	Direct	10 Minutes at 95°C.	
10	Mercerized	Direct	10 Minutes at 95°C.	
11	Bleached oxidized	Direct	10 Minutes at 95°C.	All done with CONGO RED DYE.
12	Unbleached oxidized	Direct	10 Minutes at 95°C.	
13	Bleached tendered	Direct	10 Minutes at 95°C.	
14	Unbleached tendered	Direct	10 Minutes at 95°C.	
5	Bleached	Basic	10 Minutes at 95°C.	
6	Unbleached	Basic	10 Minutes at 95°C.	
7	Mercerized	Basic	10 Minutes at 95°C.	
8	Unbleached oxidized	Basic	10 Minutes at 95°C.	Tannic acid was used as mordant for the MALACHITE GREEN DYE.
9	Bleached oxidized	Basic	10 Minutes at 95°C.	
15	Bleached tendered	Basic	10 Minutes at 95°C.	
16	Unbleached tendered	Basic	10 Minutes at 95°C.	
17	Bleached	Mordant	10 Minutes at 95°C.	
18	Unbleached	Mordant	10 Minutes at 95°C.	
19	Mercerized	Mordant	10 Minutes at 95°C.	These samples were treated 10 minutes with boiling ferric acetate, suspended in air 5 minutes, then boiled or treated with *Alizarin* 10 minutes at 95°.
20	Bleached oxidized	Mordant	10 Minutes at 95°C.	
21	Unbleached oxidized	Mordant	10 Minutes at 95°C.	
22	Bleached tendered	Mordant	10 Minutes at 95°C.	
23	Unbleached tendered	Mordant	10 Minutes at 95°C.	
24	Bleached	Vat		
25	Unbleached	Vat		
26	Mercerized	Vat		All samples treated with a bath of 2g. indigo, lg. $FeSO_4$, and 1.18 g. CaO @ 95°C. with 4 immersions of cloth for 10 minutes with 5 minutes of suspension in air between each immersion.
27	Bleached oxidized	Vat		
28	Unbleached oxidized	Vat		
29	Bleached tendered	Vat		
31	Bleached	Acid		
32	Unbleached	Acid		
33	Mercerized	Acid		Bath of ORANGE II used for 10 minutes at 95°C. Few drops of acetic acid were added to release the acid dye. Extra acid was added after 5 minutes.
34	Bleached oxidized	Acid		
35	Unbleached oxidized	Acid		
36	Bleached tendered	Acid		
37	Unbleached tendered	Acid		
39	Bleached	Ingrain		This dye bath was made according to *ANON*, Am. Dyestuff Rep. *8*, No. 23, Sec. 2, 16-17 (1921). The constituents of the dye bath were: Water 130 grams HCl 4 grams (34° Tw.) Aniline 1 gram $K_2Cr_2O_7$ 1.4 grams The aniline and HCl were mixed with 5cc. water and added to the 130 grams of water. The chromate, dissolved separately, was added to this solution and the cotton immediately immersed. The temperature was slowly raised to 50°-60°C., and maintained for 1 hour, after the cotton samples had first remained in the cold solution for one hour. Samples were then boiled with powdered castile soap ten minutes, washed, and dried.
40	Unbleached	Ingrain		
41	Mercerized	Ingrain		
42	Bleached oxidized	Ingrain		
43	Unbleached oxidized	Ingrain		
44	Bleached tendered	Ingrain		
45	Unbleached tendered	Ingrain		

and Thompson[13] showed that tendered cotton has a marked increase in affinity for methylene blue. Birtwell, Clibbens, and Ridge[14] observed that dye absorption is partly dependent on the alkalinity of the ash, the origin of the growth, and the pectic impurities of the cotton. It was found that removal of impurities reduced the dye absorption.

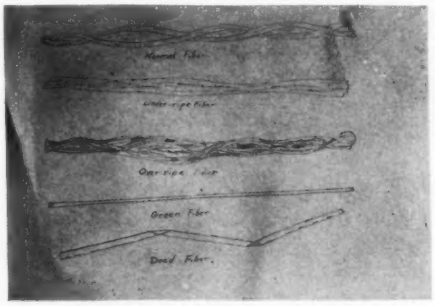

Fig. 1—Drawing showing types of fibers

This study was made to determine the behavior of the various growth condition fibers under the usual conditions of commercial treatment. It was decided to analyze under

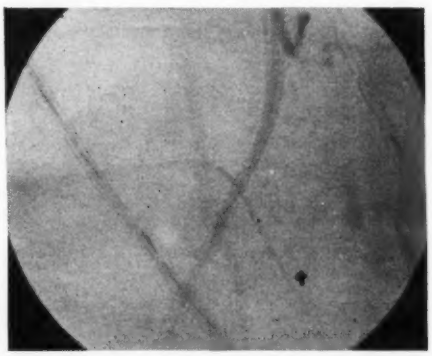

Fig. 2—Photomicrograph showing green fiber

the microscope samples which were unbleached, bleached. mercerized, unbleached tendered, bleached and tendered, unbleached oxidized, and bleached and oxidized. A dye falling in each of the usual classes of dyes was used on each sample. They were acid, basic, mordant, direct, in-

Fig. 3—Photomicrograph showing normal and over-ripe fibers

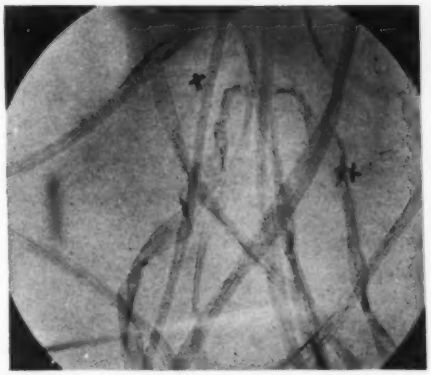

Fig. 4—Photomicrograph showing dead and under-ripe fibers

grain, and vat dyes. It was not convenient to use print dyes, but observations made on commercial fabrics indicate that statistically speaking, these fabrics gave the lowest results in dyeing efficiency.

Samples of best quality bleached, unbleached, and mercerized domestic, which were made by one of the South's leading processors, were obtained from a local retail store. Pieces of each were given the preliminary treatment, and sample strips were cut for dyeing. Table I shows how the samples were prepared. Samples for the analyses were mounted on slides with Canada balsam and cover glasses.

Several samples were taken from the original fabrics at various places and a statistical average of the quantities of the various types made. It was noted that in every sample mounted some of each type was discovered.

Results

The count of the fibers in the original cloth showed green fibers 4%, under-ripe fibers 20%, normal fibers 53%, over-ripe fibers 17%, and dead fibers 6%. An examination of the finished fabrics showed a slight decrease in the percentage of green and dead fibers.

The results of the examination of the dyed samples are given in Table II. The appearance of the fibers was arranged to show the effect of each dye upon each type.

Green fibers failed to dye properly under any of the conditions given. The best results were obtained from the direct dye. It has been suggested by Clegg and Harland[15] that the imperfect fibers were really dyed, but their optical properties made them seem not to be. There is some foundation for this conclusion, particularly if transmitted light is used in the examination, but observation of a great many samples both by reflected and transmitted light indicated that there is actually less dyeing. There is perhaps insufficient data to ascribe this inability to take dye to a chemical property. Balls[16] concluded that the fiber first developed a cuticle into which the normal fiber later developed, and that this cuticle may or may not

[13]Jour. Soc. Dyers & Col. 1921, xxxvii 270.
[14]Jour. Text. Inst., 1923, xiv. 227.
[15]Jour. Text. Inst., 1923, xiv. 125.
[16]Phil. Trans., 1915B, 1915.

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Washington News Letter

The Federal Trade Commission as a Guardian of Color and Design

By WALDON FAWCETT

QUITE aside from its fresh responsibilities under the NRA Code system and other aspects of the New Deal, the Federal Trade Commission has an influential function as a guardian of original design in industry and of color, distinctively used. Moreover, the socalled "supreme court of business" is continuing the exercise of this regulatory power coincident with its added activities. And, as though these multiple applications of its censorial power were not enough, the Trade Commission is, coincidentally, carrying on investigations of commercial conditions that, alike to the research by the U. S. Tariff Commission, are of informative value to science and industry.

If chemists and members of the dye industries have, in any measure, overlooked or underestimated the resources of the Trade Commission as a champion of priority in industrial development it is perhaps due to the direction of the trade body's approach to this subject. The Trade Commission has no concern with patents (including design patents) as such. Nor does it undertake to determine what constitutes trade mark infringement, misbranding, or misappropriation of technical trade terms. Commercial police work by the Federal Commission is wholly the complement of its obligation to prevent unfair trading and suppress unfair methods of competition.

One vital detail of the workings of the Trade Commission machinery is often missed by observers. To incur interference by the board it is essential that the public interest shall be involved. Although, ostensibly, the Trade Commission, in every remedial program, proceeds on its own initiative, in reality its attention is usually directed by an interested party to alleged irregularities in business competition. A preliminary and more or less informal investigation is the sequence following receipt of a confidential protest and the test of "public interest" is immediately applied. Presumably, the Trade Commission will never take a hand in a private controversial issue that is essentially a dispute born of the rivalry of two or more individual business interests. The position taken by the Commission is that where an alleged violation of the law is a purely private controversy, the aggrieved party must seek redress in the courts unless the offending practices tend to affect the public.

Vindication of private property rights in color and creative design by the Trade Commission may be accomplished in two ways,—with direct and indirect operation, respectively. On the one hand, there is the summons—and—mandate formula. When, following a preliminary investigation, ground is found for intervention by the Trade Commission a Complaint is issued requiring the indicted party to show cause why he should not be required to halt his infractions of the legal code of fair competition. Then, in the natural order, follow the taking of testimony, filing of briefs, oral argument, etc. When all the evidence has been digested the Trade Commission disposes of the case either by a formal Order of Dismissal or by a Cease-and-Desist Order requiring abandonment of the stipulated practices.

In contrast to this individual and direct attack upon violation of business principles, is the moral suasion which the Trade Commission applies to industrial groups, via what is known as the Trade Practice Conference. The get-together-for-the-common-good mechanism is a device for collective or cooperative regulation of trade practices of doubtful legality or propriety. Foregathering in the cause of mutual reform, the representatives of an industry may assemble voluntarily or at the invitation of the Trade Commission. Whatever the inspiration, the Trade Practice Conference is under the auspices of the Commission, albeit every opportunity is afforded the members of industry for confidential exchange of opinions in executive session. The purpose is the consideration of any unfair practices common to an industry or a considerable section of an industry. And the agreement upon and provision of means for abandonment of the disapproved practices. The housecleaning to be carried out with the aid and support of the Commission.

The scope of color control, as exercised by the Federal Trade Commission under Section 5 of the Federal Trade Commission Act, is illustrated representatively by the action in the case of J. Merrell Redding of Dallas, Texas doing business as Ethyl Gas Company. After the routine of investigation the Commission reported "Findings of Facts" which, among other charges, laid the accusation that this respondent had so colored his product that when mixed with gasoline the ultimate product was similar in coloring and could not be distinguished from the product of the Ethyl Gasoline Corporation of New York, thereby deceiving and misleading the purchasing public. Accordingly, an Order was issued requiring Redding to cease and desist from confusable uses of color, including duplication of color in the "dress" of gasoline pumps, signs,

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JULY 16, 1934

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Quality of Water for Textile Mills and the Treatment of Their Wastes*

By **EDMUND B. BESSELIEVRE**
Member Amer. Soc. C. E. Sanitary Engineer, The Dorr Co., Inc., N. Y.

AN ABUNDANT supply of clear, soft water is as much one of the raw materials of textiles as the cotton, or the dyes. It enters into the cost of production to an extent which has not been always properly evaluated and in numerous cases can easily mean the difference between profit and loss.

The ideal condition that any textile man can visualize is, of course, a suppy of water, clear and sparkling, free from chemical compounds, which runs into the mill without any form of treatment being necessary. Sorry to say there are very few such sources available anywhere and due to the community spirit adopted by textile mills in congregating in sections, the chances of finding such unadulterated supplies are practically nil.

It will be the effort in this paper to discuss the ways that may be taken to procure a sufficiently clear supply of water at the least expense and to discuss in the latter part the ways in which pollution of supplies by the wastes from textile mills may be abated or prevented.

Water, for textile mill use, should be free from

1. Turbidity
2. Iron
3. Sulfur and other chemical compounds
4. Hardness.

*Presented at meeting, Piedmont Section, Greensboro, N. C., January 27th.

I refer, of course, to the water as it goes to the kiers and process kettles. The raw water may contain all of these deleterious components and still be made usable, at a price. The cutting down of that price is the essential thing. In general it may be done in two ways.

First: by extensive chemical treatment

Second: by proper conditioning or preparation.

To determine which of these will be the cheaper in a given problem is, of course, a matter of study and investigation and should be handled by a competent engineer with experience in handling and solving textile mill water problems, the plant chemist, and the owners. These three elements in whole hearted cooperation can usually bring forth a result that will justify the cost of the technical advice employed.

There are several factors which tend to make extensive chemical processing of water the least desirable of the two methods, even though, in some cases it may turn out to be the cheapest. Iron compounds used in a water, which later is to be used in the dyeing operations, may cause spotting of the cloth and the ruination of many yards of goods. Sulfur compounds on the other hand may cause chemical compositions with the dyes and cause streaking and also will give trouble in the boiler plant causing later expense in that department. Excessive calcium compounds may increase the hardness of the water to a point where it affects the cost of soaps used to an appreciable degree. The reduction, or elimination, therefore of chemical dosages would seem to have beneficial effects, not to mention the actual cutting down of daily operation expense due to chemical costs and the reduction of labor costs in the simplification of the control factor.

Many textile mills use a million gallons of water a day, many of them use many millions. Considering that one grain of alum per gallon totals 143 pounds of alum per million gallons, and assuming that this alum costs $0.0125 per pound, it is simple to figure that any mill can save $1.79 per day per million gallons of water used by merely reducing the alum dosage 1 grain per gallon. And that is not an impossibility in many cases. Other chemicals may be reduced in proportion, of course, as the full usage of those used is made possible by the proper preparation of the water before it passes to the filters or the final settling tanks.

Practically all turbidity may be removed by adding enough chemicals, but here again there is an economic balance which I believe can readily be swung in favor of preparation. The addition of chemicals is a daily charge and an appreciable one and if capitalized in most cases will show a startling reason for perhaps a little more initial investment in equipment. The savings made by such investments may often pay for the investment itself in a short period of time, and at the same time cut down the operating charge of the plant.

There are many textile mill water plants which may be revamped to produce better waters by the adoption of some of the modern methods of preparation which have been developd for municipal water treatment plants, at very little cost for changes in structure and a minor investment in equipment.

Proper preparation, or conditioning of the water, means simply getting the maximum value from the chemicals added, thereby cutting down the amount needed, making use of simple means to procure maximum flocculation, flexible means for adapting the conditioning apparatus to the needs of the case, especially where the water supply is "flashy" and subject to rapid or periodical change. How can this be done?

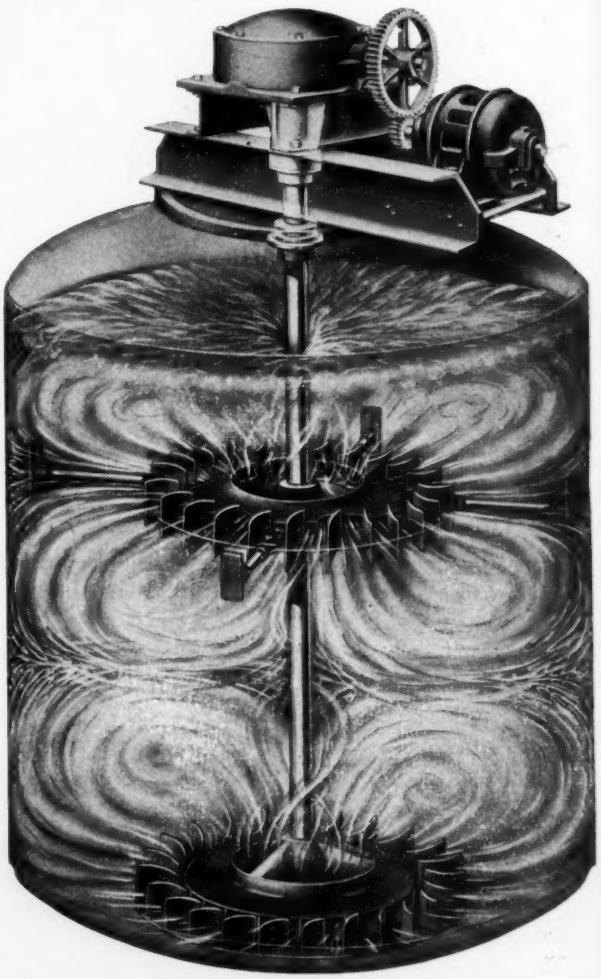


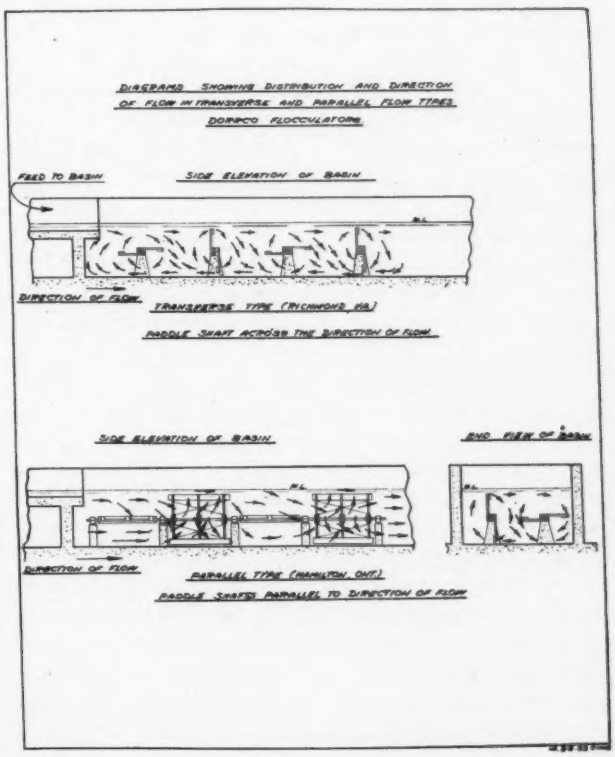
Illustration of Agitation in Turbo Mixer

It is well known that by laboratory tests, usually with a small stirring mechanism of some kind, the amount of chemicals required to produce a floc in a given water are readily determined. Usually, however, the laboratory practice is not carried out in the plant itself, due to in-

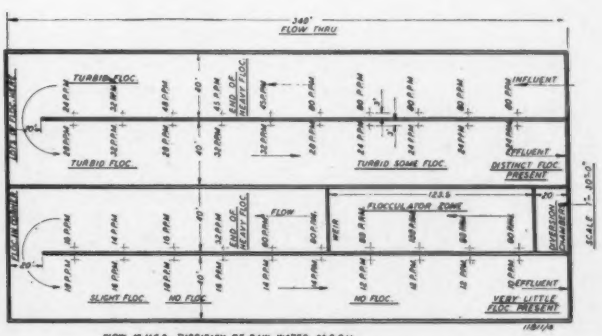
adequate equipment or ineffective arrangements. Thus, it has been found that it is either necessary to increase the dosage or bad water is sent to the filters with the result that filter runs are cut down and the cost of operation goes up. Modern developments have shown that certain types of mixers, now available, may be installed, which will provide an instantaneous and intimate mixture of the proper amount of chemical so that floc will be formed in the minimum of time, say not over ten minutes, and usually less, and may be passed on to the succeeding step. It has actually been found, in many cases, that a unit which is in effect a centrifugal pump impeller mounted on a shaft, and rotated rapidly, with a ring of vanes mounted outside of the periphery of the rotating impeller, produces the most active mixing, and by causing what is known as a "torroidal" roll of the water produces intimate mixture in every few minutes. This unit is known as the Turbo Mixer and the accompanying slides illustrate its general structure.

Following the "flash mix" which assures maximum usage of the chemicals added and produces a floc in a manner and time which will frequently better the laboratory test, we believe that these flocs should not be allowed to settle without further attention but they should be nursed and coaxed into becoming highly adsorptive of their smaller brothers. Rapid growth is not necessarily synonymous with strength, but in the average floc produced by chemical treatment of water it can be made to increase in size and settling qualities by proper steering in its passage through the flocculation zone.

That, in effect, is what is now done in a unit known as the "flocculator," a unit developed in the last three years and which has made great strides in introducing economies to municipal and industrial water plants. The entire theory of this unit is that it picks up the small floc formed in the mixing tank and passes them around through all zones of the water in the coagulation basin, thus causing them to adsorb the finer particles floating around and finally at the end of the flocculation zone the flocs are gently released from their handlers and are allowed to settle to the bottom of the tank. In other words, instead of allowing the flocs to follow a straight course from the inlet end of the basin to the outlet and pass by many of the finer particles, the "flocculator" provides that each floc shall, as far as possible, take a zigzag course in its journey, upwards, downwards and side-wise, so that it will sweep through every part of the body of water and pick up the maximum of fine particles.


DIAGRAMS SHOWING DISTRIBUTION AND DIRECTION OF FLOW IN TRANSVERSE AND PARALLEL FLOW TYPES DORRCO FLOCCULATORS
FEED TO BASIN
SIDE ELEVATION OF BASIN
DIRECTION OF FLOW
TRANSVERSE TYPE (RICHMOND, VA.)
PADDLE SHAFT ACROSS THE DIRECTION OF FLOW
SIDE ELEVATION OF BASIN
END VIEW OF BASIN
DIRECTION OF FLOW
PARALLEL TYPE (HAMILTON, ONT.)
PADDLE SHAFTS PARALLEL TO DIRECTION OF FLOW

Dorrco Flocculators at Richmond, Va.



FLOW, 48 M.G.D., TURBIDITY OF RAW WATER, 65 P.P.M., CHEMICAL DOSE 0.8 GRAINS OF ALUM PER GALLON.

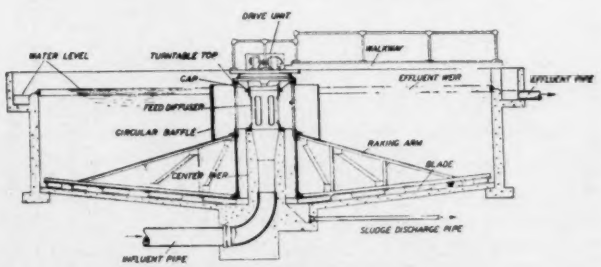
LOUISVILLE WATER COMPANY
FLOCCULATION TESTS SEPTEMBER 14, 1933.

After this flocculation stimulation has been carried on for a given period, it is gradually reduced so that the flocs having been formed are released without tendency to facture. The application of this principle is illustrated in the slides shown, which show, not only the general principle of operation but the form of mechanism used and its adaptability to existing plants.

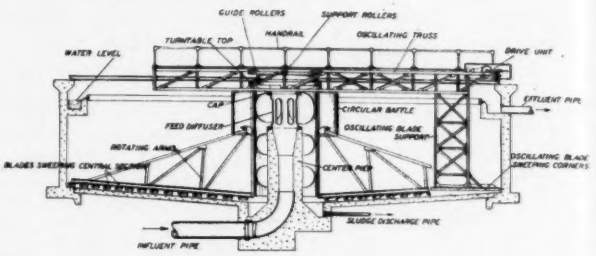
It can readily be seen that by this means of preparation, the chemicals added are made to produce their maximum effect and that chemical cost may be materially reduced in many plants. In other plants, where the chemicals now used are close to the optimum point for obtaining a floc, it usually is possible to obtain a better water for application to the filters, even though the amount of chemical may not be reduced to any appreciable degree. This again may readily be translated into savings and extra profit on the production cost of the goods. If by proper preparation, the filter runs may be doubled, as is frequently the case, considerable time is saved in labor during backwashing, the capacity of the plant may be increased, and the saving in backwash water cut in two, and this in itself is no inconsiderable item, especially if the backwash water is pumped, as is usually the case. Pumping half the volume will cut down the pumping cost by the same proportion. These items capitalized frequently run into large sums.

A third item of proper preparation which is reflected directly into profits is the cleaning of the basins. The water which passes into the sedimentation basins is chemically treated and may be worth, due to that reason, alone, a considerable sum. If, due to the accumulation of sludge in these basins their capacity is affected and decomposition of organic solids affects the quality, they must be emptied at periods to be cleaned and the treated water in the basin is lost. By providing mechanically cleaned sedimentation tanks following the flocculation step this loss may also be eliminated, as this newer type of basin never needs emptying. The following slides illustrate the most generally used type of unit for this purpose.

The expense of installation of any of these units is small and the savings to be made are large and the consideration of adapting these methods of preparation to any new or old plants is warranted. Incidentally, the adoption of proper preparation may mean an initial saving of plant structure that will more than compensate for the expense of the equipment, as by providing a better water after the flocculation step, the sedimentation basin size may be reduced materially from the size previously considered necessary and as these basins have been in the past built for holding from 6 or more hours' flow of the water a material reduction in their size makes a large saving.



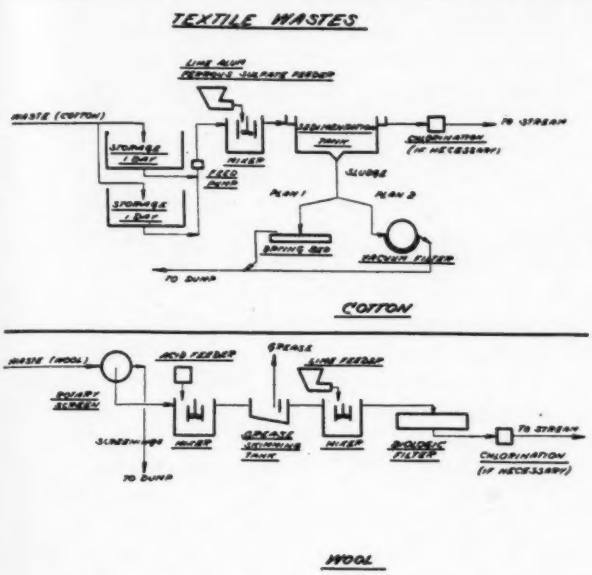
THE DORR CLARIFIER
SIPHON FEED & CENTRAL DRIVE
PATENTED



THE DORR CLARIFIER
SIPHON FEED & TRACTION DRIVE

Treatment of textile mill wastes is not so simple as the treatment of the water for production. However, there is room for a great deal of cooperation between mills in this respect, which if given friendly consideration might save both parties much money.

It is frequently the case that one textile mill will discharge its wastes into a stream which a mile or so further down is used as a source of water supply for another mill. Naturally, the mill owner faced with a problem of waste treatment wants to get out as cheaply as possible, as this must be carried as an unamortized charge against his cost of production. He usually thinks little of the effect his waste discharge may have on the mill owner below in endeavoring to use that same supply for his mill processes. He may find that he can so treat his wastes by chemicals, at a minimum expense, that he gets off within his limit of expectation, but on the other hand, those same chemicals may make the stream water so bad for the man below that he will have to install a very complete water treatment to prevent spoilage of his goods by the chemicals added by his neighbor. Getting together to consider these factors might result in the development of a treatment method on the one case which would result in a moderate water expense for the man downstream. It is not too Utopian to anticipate that it would pay these two men to get together and work out a system which might cost the upstream man a little more for his waste treatment, but on the other hand reduce the extent of treatment for the man below. And to compensate the man above for his extra expense the man below pay whatever additional cost is required over and above the cheapest treatment for

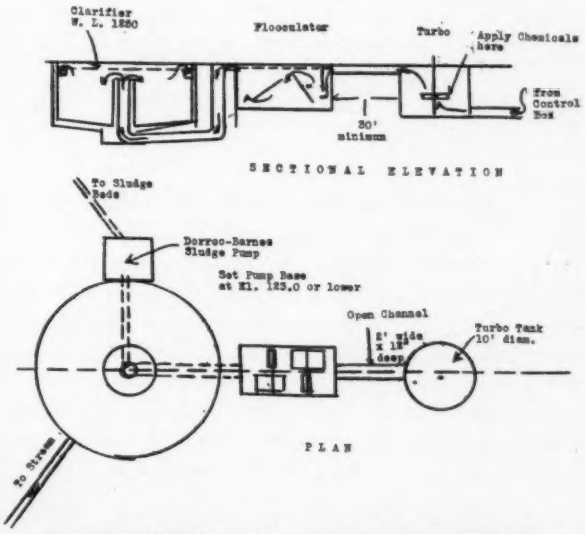


the waste plant. An ideal arrangement would be for them to keep a joint account for their waste and water treatment and each to pay half the bill.

In many cases, both the plant owner having a waste problem and the downstream man having a water problem, may be benefitted by a check-up on plant operations and the entire elimination of certain wastes. In other instances, some of the less obnoxious wastes may be diverted to other outlets than those used by other mills as water supplies and only the most obnoxious wastes treated. In other cases, the reverse is true, that large volumes of non-polluting wastes may be used for their reaction on the polluting wastes and for their value as diluents.

The ideal plan for a textile mill area, where there are a large number of mills in a short radius would be to form a Water and Waste Commission, which would formulate plans for treatment and a diversion of wastes to sources not being used by their own or other textile groups and to have a joint plant for water treatment. In general this plan would result in economies to all, provided the mills are located sufficiently close together as not to require excessive lengths of sewer or water service main.

Textile wastes, particularly those from mills treating cotton goods, may be economically treated in a plant of moderate expense and turn out an effluent which will not pollute adjacent water supplies used by other mills. This treatment involves a careful study, by experienced technicians, of the problem, of its relation to adjacent industries, the source of the wastes and the availability of local supplies of chemicals. In general it is best to utilize chemicals which are readily procured on any market rather than proprietary compounds which are sold only by one or more producers. The overall cost of the use of common chemicals is usually less than when other special compounds are used, although this may not always be true particularly if the subject mill is near the source of manufacture of the special compound. To utilize the chemicals to their maximum degree of efficiency it is essential in a waste plant, even more so than for water treatment, to provide proper preparation of the wastes for the succeeding treatment. The slide shown illustrates a plant recently constructed and its utilization of modern methods of preparation and treatment. The various wastes are concentrated in a separate basin for each in order to maintain a uniform character of waste these wastes are fed to a combined waste flow by means of proportional weirs.



Flowsheet of Typical Plant for Treatment of Textile Mill Waste

This waste is then fed to a "flash mixer" where the chemicals are fed and given the intimate mix and then flow to the flocculator where the floc will be built up to the maximum. Next they go to the "clarifier" where the color will be settled out and the sludge collected mechanically and sent to drying beds. This treatment should produce an effluent practically free of color as it leaves the plant and when diluted with the adjacent stream water will entirely disappear. The effluent will contain nothing detrimental to the use of the stream by adjacent farms or downstream mills.

Textile mill wastes are complex, but by intelligent study of the problem, adjustment of flows of the individual wastes so as to obtain the reactive value of each to the other, and by usage of modern means for handling and treatment, such plants may be developed and built at costs within reason and which will operate at a minimum cost for labor and chemicals.

In water treatment for textile mills and the treatment

of the wastes from them, much benefit can be derived from obtaining the advice of three factors:

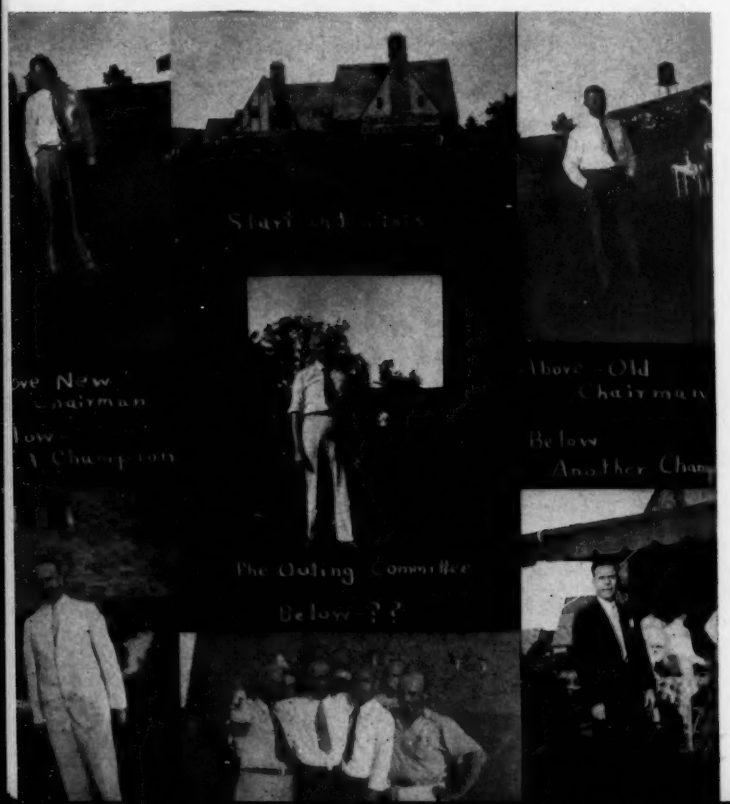
1. The plant chemist, who can provide valuable assistance and data on the character of water sources, the character of water desired and other plant data.
2. The consulting advisor who with his wide experience in solving similar problems elsewhere has gained a wide knowledge of conditions, the ways to cut corners and is posted on the modern facilities for obtaining the maximum of result at the minimum cost, and
3. The state department of health, which will give valuable data on stream flows, analyses of water, the necessity for measures for elimination of pollution, the degree of treatment required, etc.

This trinity of interests, properly assembled, and with all cards laid on the table, will usually produce a result which will redound to the credit of all, and in the long run will be the cheapest for the man who pays the ultimate bill, the plant owner.

OUTING, NEW YORK SECTION

WITH special permission of the copyright owners a beautifully hot day greeted the New York Section at their outing held at the North Jersey Country Club in Paterson, N. J., on June 29th. It was rumored around that Outing Committee Chairman Arthur F. Wiehl was directly responsible for the weather but verification of this rumor was not forthcoming and some were so ungrateful as to hint that it was *too* hot.

Be that as it may the temperature was not high enough to keep those hardy warriors of the links in the locker rooms and consequently it became necessary to award the usual golf trophies. The cup for low net was again awarded to P. J. Kennedy, the up and coming new secretary of the section, thus giving him a second leg on this particular prize. As any person who wins three legs on the cup becomes permanent owner a movement was immediately inaugurated to prevent his appearance at the outing next year. His net score was 72. The Chairman's Prize for low gross, donated by Ephraim Freedman, was awarded to Henry Herrmann, the retiring chairman. It appeared for a moment that politics had entered into the golf tournament but a glance at the score sheet showed that the former chairman was entitled to the award with a low gross of 94 and a net of 76. The guest prize for the day went to Charles Sabriski of the Bluebird Dye & Print Works of Haledon, N. J., who reported a low net of 73. In addition to the prize he was also awarded an application blank for membership in the hope that his game would improve enough during the year so that he would be enabled to win a leg on the cup mentioned at the beginning of this paragraph in the event that the movement to keep Pat Kennedy away was not successful. There were many others of championship calibre who displayed their wares on the course and they were rewarded by being allowed to dine with the rest of the gathering. Among these was F. Aufrichtig who is being touted as the next open champion. Just why he did not win the low net at this tournament was not fully explained although it was reported that Arthur Wiehl has appointed himself as manager to help him triumph next year.



In a remarkable tennis tournament that started out to consist of but 3 sets but ended after 16 had been played, George Baxter, who worried about the programs all last season, emerged the victor and was forthwith handsomely decorated with a freshly picked bouquet of *Chrysanthemum leucanthemum* (daisies to you).

One of the features of the dinner hour was the awarding by lot of a set of horseshoes. It had been originally planned to hold a horseshoe pitching tournament but the followers of this sport apparently found diversion elsewhere and as the chairman refused to carry the prize home again it was raffled off. After some discussion as to whether the number drawn was a 9 or a 6 the judges held a council and Louis Zisman, holder of number 9, was declared the winner.

Arthur Wiehl, as chairman of the outing committee, was called upon for a few words so he thanked the gathering for allowing him to act in this capacity and bemoaned the fact that outings were not what they used to be in the "good old days". As a matter of fact however Arthur is entitled to a rousing cheer of gratitude for his very able efforts in conducting the 1934 outing of the New York Section.

Proceedings of the American Association of Textile Chemists and Colorists

The Photochemical

Decomposition of Silk[1]

By MILTON HARRIS[2]

The purpose of this investigation was to study the deterioration of silk on exposure to daylight under natural conditions of use.

The strength of silk cloth decreased and its ammonia nitrogen content increased on exposure to sunlight. Samples of the cloth treated with a tenth normal solution of sodium hydroxide showed smaller changes and samples treated with a tenth normal solution of sulfuric acid greater changes than the untreated cloth under the same conditions.

Similar results were obtained on exposure of samples to north skylight. Samples treated with sodium carbonate solution of one per cent or less in concentration showed the greatest stability.

The amino nitrogen content was the same for silk stored in the dark and silk exposed to sunlight for three months. The rate of hydrolysis in 0.5 normal sodium hydroxide solution, measured by the formation of amino nitrogen, was the same for both samples.

The decrease in breaking strength and increase in ammonia nitrogen content of silk on exposure to light are brought about by atmospheric oxidation in the presence of light.

The results of these experiments are in accord with those obtained in the accelerated ageing tests of silk, using the carbon arc lamp as a light source.

I. Introduction

PREVIOUS work[3] has shown that when silk is exposed to the radiation of a glass-enclosed carbon arc lamp, the extent to which it is weakened depends upon its "pH" (as defined by the pH of an aqueous extract). Silk was found to have maximum stability at about pH 10. As the pH was increased above pH 11 and decreased below pH 3, the stability of the silk decreased rapidly. Silk treated with 0.1 normal sodium hydroxide solution was more stable to the action of light than untreated silk or silk treated with 0.1 normal sulfuric acid and the latter was the least stable.

The purpose of the present investigation was to study the deterioration of silk on exposure to daylight under natural conditions of use. Both the chemical and the physical breakdown were followed. The experiments were designed to show something of the nature of the photochemical reaction.

II. Experimental

The general procedure was that used in the previous work and has been described[3]. The decrease in breaking strength of the cloth with time of exposure was taken as a measure of the physical breakdown of the silk. The chemical breakdown was followed by analyzing specimens for ammonia nitrogen and amino nitrogen. The former is that portion of the nitrogen which is liberated when the silk is boiled in a saturated solution of magnesium oxide. The latter is the portion obtained when the silk is treated with nitrous acid, using the method of Van Slyke[4].

One series of experiments was concerned with the effect of sunlight. Degummed silk was purified by successive extractions with alcohol and ether and then washed for one-half hour with water at 60°C. to remove any adsorbed solvent. Some samples of the silk were soaked in 0.1 normal sodium hydroxide solution and others in 0.1 normal sulfuric acid solution for 10 minutes. The excess liquor was removed by centrifuging and the samples were dried. Samples of purified acid-treated and alkali-treated silk were then exposed to sunlight. The exposures were continuous day and night, regardless of the weather, under glass at an angle of 45° facing south. At the end of 15 days the alkali-treated silk had a breaking strength of 53 pounds, the untreated sample 38 pounds, and the acid-treated sample 8 pounds. The strength of the original cloth was 55 pounds. At the end of 4 months the untreated and acid-treated silk had practically no strength but the alkali-treated silk still had 10 per cent of its original strength.

At intervals of time, samples were analyzed for ammonia nitrogen. The results are given in Table 1. All of the exposed samples gave increasing amounts of ammonia nitrogen with increasing time of exposure, the greatest amounts being present in the acid treated and untreated samples.

The total nitrogen content, amino nitrogen content, and relative susceptibility to hydrolysis of the purified silk (not treated with acid or alkali) which had not been

Table 1

The Effect of Sunlight Exposure on Ammonia Nitrogen Content of Silk. The Number of Milligrams of Ammonia Nitrogen per Gram of Silk Is Given.

Time of Exposure Days	*Untreated Silk Not Exposed*	*Untreated Silk Exposed*	*Silk Treated with 0.1N NaOH*	*Silk Treated with 0.1N H_2SO_4*
32	0.10	0.31	0.16	0.87
69	0.08	0.37	0.22	1.03
90	0.10	0.64	0.45	2.05
104	0.09	0.75	0.52	2.09
130	0.07	1.06	0.64	2.81
150	0.12	2.00	0.95	2.92
175	0.11	2.60	1.03	2.99

exposed to strong light and which had been exposed to sunlight for 3 months were determined. The sample for analysis was ground to a fine powder. In order to determine susceptibility to hydrolysis, about 5 grams of the powder was shaken in 200 ml. of water for 4 hours using an automatic shaker. The larger particles of silk were allowed to settle and the supernatant liquor was decanted and mixed with an equal volume of 1 normal sodium hydroxide solution. The mixture was kept at 37° C. in a thermostat. Ten ml. aliquots were withdrawn at definite intervals of time and analyzed for amino nitrogen and for total nitrogen. The results are shown in Figure 1. Neither the unexposed nor the exposed silk contained an appreciable amount of amino nitrogen before hydrolysis. The rate of hydrolysis, measured by the formation of amino nitrogen, was the same for both samples.

Another series of experiments was concerned with the deterioration of silk cloth treated with acid and alkaline solutions on exposure to north skylight. The samples were exposed continuously in a room behind window glass, vertical, facing north. Plain weave cloth weighing approximately 1.6 ounces per square yard was cut into pieces about one yard square. These were purified by

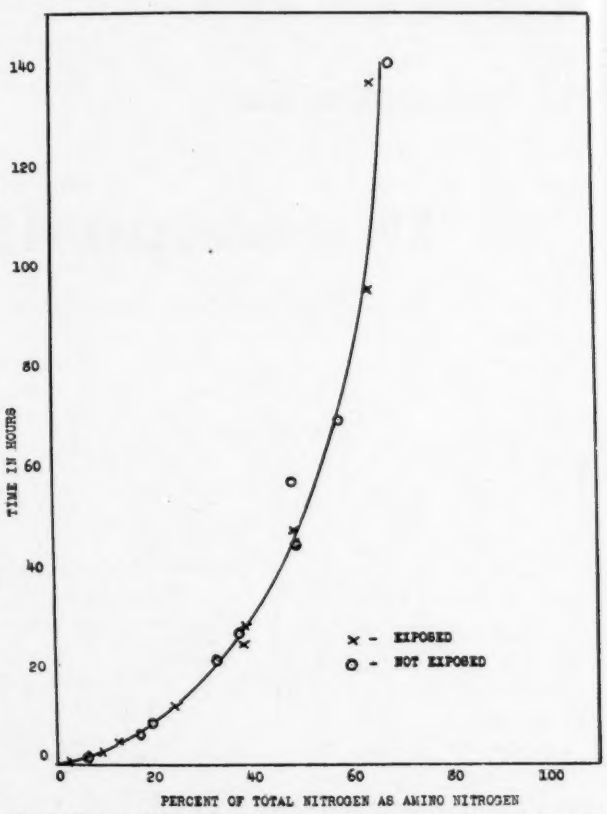


Fig. 1—The rates of hydrolysis of silk which had not been exposed to strong light and which had been exposed to sunlight for 3 months

scouring in a one-half per cent soap solution at 60° C. for 20 minutes; rinsing in three successive baths of water at 60° C. for 20 minutes each; extracting with alcohol and ether for 24 hours each; and finally washing with water at 60° C. for 30 minutes. The individual cloths were soaked for 5 minutes in the solutions listed below, centrifuged, and dried at 70° F. and at a relative humidity of 65 per cent.

Table 2

The Appearance and Breaking Strength of Silk Treated with Acid or Alkaline Solutions After Exposure to North Light

Treatment	*Appearance After Exposure for 11 Months*	*Breaking Strength (1-Inch Strip) After 5½ Months Pounds*	*7½ Months Pounds*	*11 Months Pounds*
1. None (not exposed)	No change	37	37	36
2. 0.1% Na_2CO_3	Very Slight Yellow	34	30	30
3. 1.0% Na_2CO_3	Slight Yellow	32	29	27
4. 0.5% Na_2CO_3	Faint Yellow	32	29	26
5. None (Exposed)	No change	30	29	24
6. 1.5% Na_2CO_3	Yellow	30	27	23
7. 0.75% $NaHCO_3$	Faint Yellow	28	24	20
8. 0.01N Acetic acid	No change	17	16	14
9. 0.01N Sulfuric acid	Faint Yellow	14	13	12

1. No treatment.
2. 0.01N sulfuric acid.
3. 0.01N acetic acid.
4. 0.1 per cent sodium carbonate.
5. 0.5 per cent sodium carbonate.
6. 1.0 per cent sodium carbonate.
7. 1.5 per cent sodium carbonate.
8. 0.75 per cent sodium bicarbonate.

The breaking strength and appearance of each cloth after exposure for stated periods of time are given in Table 2. The acid-treated samples showed the greatest deterioration, the untreated sample was much more stable, and the samples treated with sodium carbonate solutions in concentrations of one per cent or less showed the greatest stability. These results are in accord with those obtained in the accelerated ageing tests of silk using the carbon arc lamp as a light source.

After eleven month's exposure, samples of the cloth were analyzed for ammonia and amino nitrogen by the following procedures: Portions of each cloth were dried for six hours at 105° C. and the ammonia nitrogen determined. The silk was then thoroughly washed and again dried for 6 hours at 105° C. One-gram portions were dissolved in 20 ml. of a 50 per cent lithium bromide solution at 80° C. and the solution diluted to 100 ml. in a volumetric flask. The amino nitrogen content of each solution was determined. The results of the analyses are given in Table 3.

Table 3
The Ammonia and Amino Nitrogen Content of Silk Treated with Acid or Alkaline Solutions After Exposure to North Light for Eleven Months

Treatment	*Ammonia Nitrogen Mg. per Gram Silk*	*Amino Nitrogen Mg. per Gram Silk*
1. None (not exposed)....	0.07	1.5
2. 0.1 per cent Na_2CO_3..	.15	1.6
3. 1.0 per cent Na_2CO_3..	.15	1.4
4. 0.50 per cent Na_2CO_3..	.23	1.4
5. None (exposed)	.44	1.4
6. 1.5 per cent Na_2CO_3..	.19	1.4
7. 0.75 per cent $NaHCO_3$..	.39	1.7
8. 0.01N Acetic acid.....	.72	1.5
9. 0.01N Sulfuric acid	1.08	1.4

The decrease in breaking strength is accompanied by an increase in the ammonia nitrogen content of the silk. The amino nitrogen content does not appear to be affected during the deterioration of the fiber.

III. Nature of the Photochemical Reaction

The photochemical decomposition of silk is a photo-oxidation reaction. Skeins of 20/22 Japanese silk have been exposed in vacuum and in atmospheres of moist and dry hydrogen and oxygen to north skylight for 4 months. The skeins in the vacuum and in the hydrogen retained their original strength. Those in the dry oxygen lost about 3 per cent while those in moist oxygen lost about 10 per cent of their strength.

The increase in ammonia nitrogen content of silk during the photochemical deterioration is further evidence that an oxidation reaction has taken place. Polit and Dhar[5] have shown that in the decomposition of most nitrogenous substances ammonia is formed and the decomposition is accelerated by the presence of oxygen and light. The deterioration of wool in the carbonizing process is also accompanied by the formation of ammonia, the amounts formed increasing with increasing acid and moisture contents of the wool and with increasing temperatures in the baking oven. When wool containing sulfuric acid is stored at ordinary temperatures, the ammonia nitrogen content increases with increasing time of storage. Baking acid treated and untreated specimens of wool in atmospheres of dry or moist air, oxygen and carbon dioxide showed that both oxygen and moisture have an important influence on the deterioration of wool. Sulfuric acid increases the rate of deterioration considerably[6]. Leiben and Urban[7] found that the splitting of ammonia from amino acids and other substances proceeds much more rapidly in acid than in alkaline or neutral solutions. Schanz[8] studied the action of ultraviolet rays on egg and serum proteins. He found that the greatest change was produced by acid solution and that the reaction was accelerated by oxygen.

The experimental results of this research are in accord with those obtained by other workers in studying the action of light on protein materials. The decrease in breaking strength and increase in ammonia nitrogen content of silk during exposure are caused by the action of the oxygen in the air in the presence of light.

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[1]The work reported here was made possible by a grant from the Textile Foundation, Incorporated, to the American Association of Textile Chemists and Colorists.

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Proceedings of the American Association of Textile Chemists and Colorists

Sulfonated Oils

Their Manufacture and Composition*

By ALFRED R. MACORMAC

Chief Chemist, Textile Chemical Products Co., Greensboro, N. C.

WHEN several months ago Jack Robertson asked me if I would give a paper on sulfonating oils at this meeting, I looked at him in a doubtful manner and said, "Well, I don't really know whether I ought to or not." Jack replied, "Oh, come on; there's no secrets to sulfonating any more. Why, all the mills are doing it now." Now a statement like that just shows what most of us already know; that there is no connection at all between selling peroxide and sulfonating oil. Let me say right now that I shall not in the course of this paper give any exact formula for sulfonating any type of oil. Nor shall I go over any of the ground covered in such an interesting manner by John Sokolinski at our meeting last October. Nevertheless, I hope that my discussion will be interesting and helpful to some of those present.

Modern chemistry has revolutionized many phases of our everyday life and no more striking examples of this fact can be given than by calling attention to some of the old sayings that are no longer true. You have probably heard the expression "You can't make a silk purse out of a sow's ear." Six or eight years ago a silk (i. e. rayon) purse made from a sow's ear (gelatine) was on exhibition at, I believe, the Chemical Exposition in the Grand Central Palace, New York. The present paper deals with the methods by which another old saying: "You can't mix oil and water" has been disproved.

I propose to discuss the subject of sulfonated oils by asking a series of questions and then attempting to answer them. When I am finished I shall be glad to help anyone present to do likewise.

Naturally the first question that arises is: "Why sulfonate oils?" and the answer is to make them soluble or more correctly speaking miscible in water, in other words so that you can mix oil in water. The introduction of the sulfonic acid group (SO_3H) renders a compound more soluble in water. This procedure is a very general one in organic chemistry. An example is the vat dye, indigo, sulfonated to give an extremely soluble acid dye, indigotine. Likewise, castor oil is sulfonated to give us Turkey Red Oil, Soluble Oil, or Sulfonated Caster Oil. In the case of indigo you will note that we have changed the entire nature of the substance. A vat dye for cotton was changed into an acid wool dye that has practically no affinity for cotton. In the case of our soluble oil we do not want to do this. We wish to retain the oily and lubricating properties and yet have a compound that is soluble in water, so we sulfonate enough to render our compound soluble, but not enough to destroy its oily character. This leads to the question: "How much shall we sulfonate?" and the answer like to the one to that old question, "How old is Anna?", is that it all depends on the circumstances. If you want an oil that will give a clear transparent solution in water, you must put in more of the SO_3H groups than you do if a milky emulsion will satisfy your requirements. An oil that forms a milky emulsion will have more oily properties than one that forms a clear solution. In the case of ordinary soluble oil the aim is to sulfonate enough of the oil so that the sulfonated portion of the oil will act as an emulsifying agent and hold up the unsulfonated portion in a clear solution in water. On the other hand, to sulfonate beyond this point would result in a decrease in the oily properties of the compound. If you are using your product as a rayon-coning or throwing oil you do not care if a milky emulsion is obtained, or even if you have globules of oil floating on top of your bath. All you want in this case is sufficient sulfonation to render the oil soluble so that it can be washed off.

If it is desired to produce a product that is to be used as a carrier for mineral oils or other raw oils, it is advisable to sulfonate to the highest possible degree. In this case there is no objection to destroying the oily nature of the oil and the greater the sulfonation the more raw oil it is possible to emulsify. However, the production of very highly sulfonated products is generally economically unsound. Special apparatus, special cooling devices, long reaction time and the expense and difficulty due to the use of special agents such as chlorsulfonic acid, sulfur trioxide and phosphoric anhydride make the process

*Paper read at Spring Meeting, Piedmont Section, A. A. T. C. & C., May 19, 1934.

expensive. In some cases the infringement of patent rights might also be involved. Procedures of this type are used in the production of the recently developed aliphatic sulfonated alcohols and esters, such as Gardinols and Avirols. The aliphatic alcohols are more stable products than the fatty acids, hence they are harder to sulfonate, but once sulfonated the resulting compounds are likewise stable. Thus, these newer sulfonated alcohols will stand up better in an acid bath and in hard water than the sulfonated fatty acid derivatives. However, the alcohol derivatives are considerably more expensive and the question of relative money value is the deciding factor in their use.

Complete Sulfonation?

This discussion of how much shall we sulfonate brings up two questions that can be answered very briefly. First, "What is there in this talk about a highly sulfonated or a completely sulfonated product?" My answer is: Just sales hooey by a high pressure salesman who knows little of the chemistry of sulfonated oil talking to a mill man who knows less. In regard to this (a completely sulfonated product) I am reminded of Lewis Carroll's remark about a purple cow, "I have never seen a purple cow, I never hope to see one, but this I tell you anyhow, I'd rather see than be one." Carried to its logical conclusion a completely sulfonated product would be one in which all the H's directly connected with the C's were replaced by SO_3H groups. Thus a completely sulfonated olein would be $(C_{17}(SO_3H)_{33}(COO)_3\ C_3(SO_3H)_5$.

Of course it is not hard to figure how this myth of a completely sulfonated oil started. Some mill man gets a soluble oil that isn't completely soluble. He raised the devil. His source of supply says "All right, we'll give you a more completely sulfonated product." They do, and it works fine. The obvious conclusion is that the higher the sulfonation the better the product will work. The conclusion is wrong of course, but the salesman doesn't know it, and if the customer demands a completely sulfonated product, he will tell him he has one.

Second, if there is no such thing as completely sulfonated oil, how about the material which is sold as 75% sulfonated castor and 50% sulfonated castor? Are they really what the name implies? Most of you can answer that question. No of course they are not. 75% castor contains about 7.5% SO_3 and 62 to 63% fat by weight and a 50% contains about 5% SO_3 and 42 to 43% fat by weight. Well then why call it a 75% sulfonated castor? My answer is because after the oil has been sulfonated 25% water is added so that the compound as bought contains 75% sulfonated castor and 25% water. How then do you get an analysis 62% fat? Because on analysis this 62% fat is weighed as free fatty acid whereas in figuring the 75% sulfonated castor the glyceryl ester of the acid was used. Most 75% soluble oils will test around 25% water. The SO_3 content will generally be under 10%.

Procedure

What is the procedure in sulfonation? Briefly the making of a soluble oil consists in treating the raw oil with sulfuric acid, washing out the excess acid and neutralizing the oil. That sounds very simple but it isn't as simple as it sounds because of the complexity of the raw oils. Each oil must be treated differently. Some are much more difficult to sulfonate than others. Sulfonation would be a much easier process if the raw oils were simple glycerides of one fatty acid but of course they are not. Castor oil contains the mixed glycerides of ricinoleic acid, oleic acid, linoleic acid, stearic acd and dihydroxystearic acid. Triricinolein which exist in at least two isomeric forms composes from 80 to 90 per cent of the oil. Olein apparently does not occur as such but the oleic acid is present as a mixed glyceride dioleoricinolein. Thus castor oil which is comparatively easily to sulfonate contains the glycerides of five different acids. This is not the place for a detailed discussion of the chemical changes taking place during the process of sulfonation. I merely wish to call attention to an important fact to which most people do not give sufficient consideration. The raw oils which are sulfonated are not simply definite chemical compounds like common salt, cane sugar, or water. They are mixtures of moderately complex organic compounds like butter and soap. Because of this fact sulfonation is not a simple chemical reaction. Several side reactions are almost certain to take place such as polymerization, saponification, hydrolysis, and formation of lactides and lactones. But we have to take what nature gives us and do our best to get a uniform product by controlling the other factors.

Let us now consider the next question. Aside from the raw oil what other factors influence the process of sulfonation? I think it can safely be said that temperature and time are the most important factors. As far as temperature is concerned it will differ with the oil used, the size of the batch, and the dimensions of the sulfonator. Thus no fixed temperature can be given, but it should be high enough to keep the oil liquid, but low enough to keep it from burning or polymerizing. As to time sulfonating should I believe be done as quickly as possible consistent with temperature control; however, from three to eight hours is necessary. The acid must be added slowly to prevent the mixture from getting too hot. Under ordinary circumstances and N. R. A. rules it takes from one to three days to complete a batch of sulfonated oil. This of course includes washing and neutralizing.

Other important factors are (1) acid strength, (2) washing solution and (3) caustic strength. As to the

acid a 66° Be. sulfuric is generally used. In a few cases a weaker acid will work successfully. More frequently a stronger one is necessary, i.e., a fuming sulfuric acid containing a varying percentage of SO_3. For instance if the oil being sulfonated contains many hydroxyl groups and a few double bonds considerable water will be formed in the process and the SO_3 will be needed to combine with this water to prevent dilution of the acid. In some cases chlor-sulfonic acid is used. In washing either water, sodium chloride solution or glauber salt solution is used. I prefer the latter. By its use the ionization of the H_2SO_4 is cut down to a minimum due to the high concentration of the SO_4 ions from the Na_2SO_4. Thus there is practically no active acidity in the solution to cause trouble. Likewise the replacement of the SO_3H group by the OH group is minimized, in addition both NACL or NA_2SO_4 solutions will prevent the formation of emulsions and give a quicker separation of the oils. The use of plain water it seems to me would lengthen the process and also change most of the SO_3H groups into OH groups. Of course it might be true that for some purposes the hydroxy acids are preferable to the sulfonic acids, and then washing with water might be the best process.

As to caustic soda (the most generally used alkali) the concentration is again important. The aim here is to neutralize the H in the SO_3H group only. The NaOH should not be strong enough to saponify the glycerine and form a soap. I believe the forming that has been giving trouble in some mills is due to too much soap in a sulfonated tallow. Neutralization is of course an exothermic reaction and so provision must be made at this stage to keep the temperature down. High temperature here would of course increase the saponification of the glyceride.

For special purposes caustic potash, ammonia, triethanolamine or other alkalies may be used for neutralization but they are all more expensive than soda. Ordinarily neutral means neutral to pheuolphthalein that is giving a slight pink color. This would be a pH of 8.3 to 8.5.

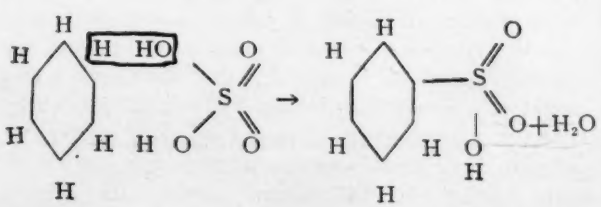
We have considered briefly how sulfonation is done and what factors need special care. Now let us consider what oils can be sulfonated.

No hard and fast answer can be given to this question. Most concerns making sulfonated oils sell sulfonated castor, corn, olive oils and tallow. These are or rather have been the most important. Vander Worth in his book lists as raw materials capable of sulfonation aromatic compounds, fatty acids and their derivations and mineral oils. I believe I would be safe in saying that any oil containing a hydroxyl group or a double bond could be sulfonated with comparative ease at those points. I am inclined to think the sulfonation of the hydroxyl is easier than sulfonation of the double bond. Thus castor oil which has a higher acetyl number of 150 seems to give the least trouble of the oils mentioned.

What is a Sulfonated Oil?

Gentlemen, I hope that so far I have impressed you with my knowledge of the subject of sulfonated oils because in my discussion of the next question I am going to admit I know very little. The question is: What is a sulfonated oil? By this I mean how does its chemical formula differ from that of the raw oil? Well frankly, gentlemen, I don't know. I've read a lot about it and discussed it to a considerable extent but—well I am like the hero of the Rubaiyat of Omar Khayyam: "In youth I eagerly did frequent doctor and saint and heard great argument about it and about, but even more came out as the discussion of the composition of sulfonated oils the same door where in I went." In other words as far as the discussion of the composition of sulfonated oils goes Mark Twain's remark about the weather when he said "Everybody talks about it but nobody accomplishes much", fits the situation very nicely. However, I believe a short discussion of some of the points involved would be beneficial Sulfonated oils all contain the SO_3H group. This group may be joined to an organic compound in two ways. First, by a direct carbon to sulfur bond. Second, with an oxygen betweeen the carbon and the sulfur. An example of the first type known to all who have studied organic chemistry is benzene sulfonic acid. Nekal, alkanol, neomerpin are trade names for compounds of this type. They are sulfonated naphthalene derivatives and are used as wetting out agents. The usual method for the determination of SO_3 is not suitable for such products. The new Hart gravimetric method must be used.

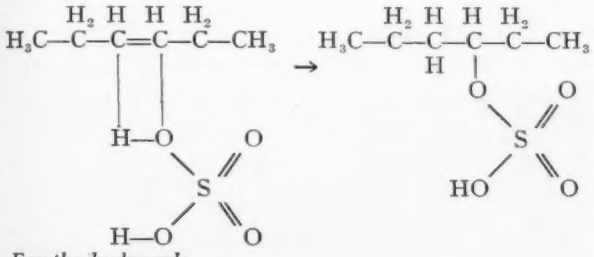
To illustrate this bond by a simple example when benzene and sulfonic acid react to give benzene sulfonic acid a hydrogen from the benzene and a hydroxyl from the acid united to form water and the rest of the two materials join to form the benzene sulfonic acid as follows:



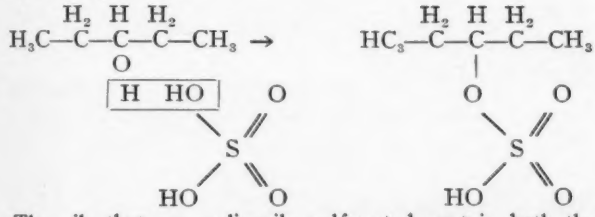
Thus the carbon and sulfur are joined directly with each other.

All of the ordinary sulfonated oils as well as the recently developed fatty alcohol sulfates such as Gardinols, Avirols, Igepons and Sulfonole are of the second type. They are really esters of sulfuric acid. In this case the organic radical take the place of a hydroxyl radical in sulfuric acid but there is an oxygen between the sulfur and carbon atoms. Sulfonations of this type will ordinarily occur only when the raw oil contains a hydroxyl group or a double bond. Graphically the reaction may be represented as follows:

For the double bond:

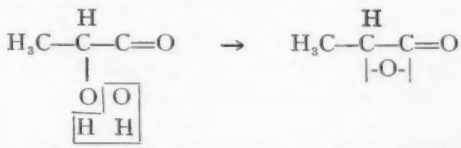


For the hydroxyl:

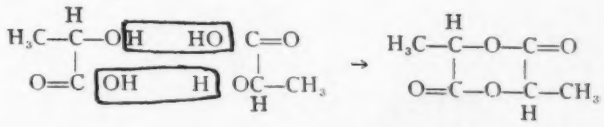


The oils that are ordinarily sulfonated contain both the hydroxyl and the double bond and sometimes several of each. That's where the fun starts and the whole mess begins to get complicated. I know of no simple method of finding what proportion of the So_3H replaces hydroxyls and what double bonds, and which of several of these groups are replaced. Of course, the iodine number will give you a measure of the number of double bonds and the acetyl number a like measure of the hydroxyls. I have no doubt but that careful determinations of the iodine and acetyl numbers of raw and sulfonated oil would give much useful information, but as control methods they are not very practical. Thus the first question that must be answered in considering the chemical formula for a sulfonated oil is what proportion of the sulfonic group has replaced the OH and what proportion has replaced the double bond? If castor oil was pure triricinolein which it isn't, and if no other reactions take place, another "condition contrary to the fact", the problem would not be especially complicated to solve by means of the determination of iodine and acetyl number as I mentioned a moment ago. Thus it is apparent that considering only the simplest change in the constitution of an oil on sulfonation we run into considerable complications.

There is one other reaction that apparently takes place during sulfonation that I should like to consider briefly. This reaction is the formation of lactones and lactides. These terms are names for two series of compounds both formed in their simplest form from lactic acid. Lactic acid contains both a hydroxyl (basic) and a carboxyl (acidic) group. Such compounds have a tendency to split out water. If one molecules of lactic acid is involved we have a lactone as follows:



This compound is an inner ester. If two molecules are involved in a similar reaction we have a lactide as follows:



Similar compounds are formed wherever we have basic and acidic groups. Thus with sulfonated triricinolein we have the possibility of a similar formation from the hydroxyl and sulfonic or carboxyl groups. There is considerable evidence that polymerization takes place during sulfonation and it is probably along some such lines as just explained. Just exactly how this change takes place or to what extent I don't know and what's more I haven't a very good idea of how to try to find out.

I have tried to explain briefly how two of the most important reactions in sulfonation change the structure of the molecule. There are several other possible reactions that take place to a greater or less extent. The oxidation of the oil is one that is frequently indicated by the odor of SO_2. Others are the decomposition of the glycerides, formation of soaps, and hydrolysis of the sulfonic group. Each of these reactions will introduce additional complications, but I think I have said enough to show you that the question just what is the chemical formula for a sulfonated oil is something that would be difficult to answer.

If all this is so what is the practical man that must get out production going to do? Well I'll tell you. He is going to get a uniform source of supply of his raw materials. He is going to check them by some one or two simple tests such as specific gravity and free fatty acid content. He is going to determine by trial and error the correct amount of acid to add. He is going to watch his temperatures so that the mix keep liquid, yet does not

burn. He is going to check his final product by some such simple test as solubility and pH; and first last and all the time he is going to count on old Lady Luck.

In conclusion let me give you one or two of my ideas in regard to the question. Will it pay a mill to make its own sulfonated oils? Before I do so I want to call your attention to the fact that I am employed by a firm that is selling sizes, oils, soaps, and other similar products to the textile industry. Therefore, it might be well to discount my advice to a certain extent. In the case of most of these products their manufacture by a textile mill is in my opinion economically unsound. Let me explain what I mean by this. Suppose a concern used a small amount, say 500 lbs. a week, of a certian sulfonated oil and suppose the process of sulfonation in this case involved the use of an inert solvent (necessitating a solvent recovery system) and fuming sulfuric acid. The equipment needed here would be expensive and probably cost several thousands of dollars. Since only a small quantity is usd it would not pay to make this product. However in some other cases I believe a considerably saving can be made. Take for example the making of a soap, let us say a tallow soap, and let us further assume that the mill does not object to the presence of glycerine in the soap and can use it in a liquid or paste form. Here we have what I consider an excellent example of an economically sound proposition. If a mill bought such a soap it would have to pay freight on a lot of water or pay for the rather expensive process of salting out and refining. Here is a case where it seems to me a mill could make one of the textile chemicals it uses cheaper than the manufacturer could sell it to the mill. In general if a mill uses very large quantities of one single product it might pay to try to make it. However, as a general rule straight sulfonated oils are extremely competitive and the various manufacturers will take such a small profit in order to get the business that the old saying—"It's cheaper to buy milk than keep a cow," is true. Finally let me say that few mills are willing to pay a chemist to take charge of this work as much as the manufacturers pay. The result is of course an inferior product. Therefore, I say that in general the mills had better stick to their job of making cloth and let us manufacturers stick to ours. We'll both have plenty of trouble as it is.

OUTING, MID-WEST SECTION

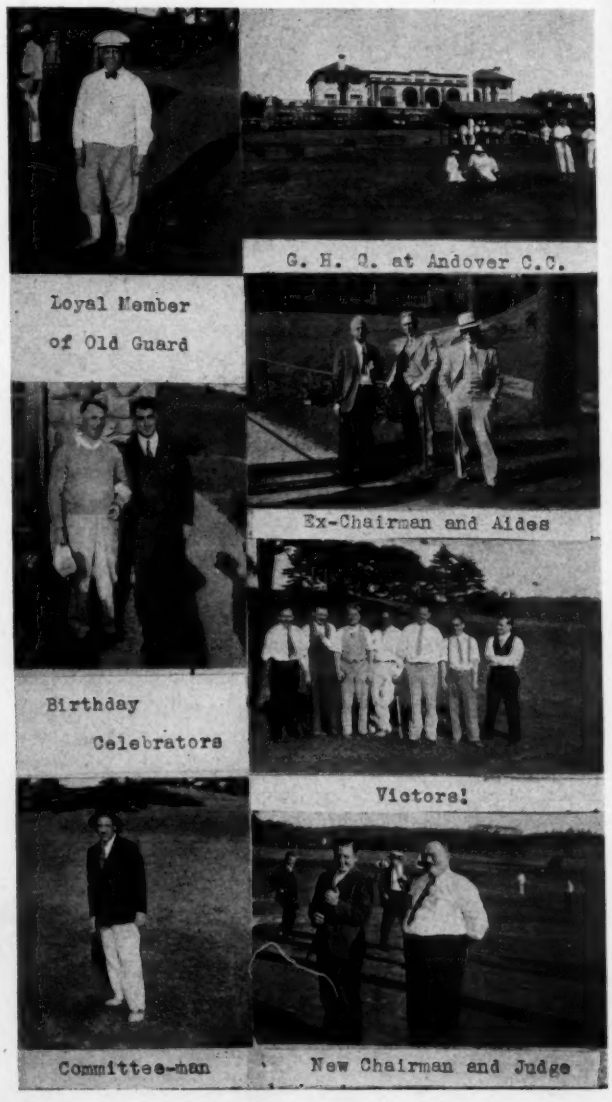
A SUMMER outing for members of this section was held on Saturday, June 23, at the Rochelle Country Club, Rochelle, Illinois. Eighty members and their guests were present to enjoy at least one round of golf and all of the good fellowship that goes along with such an event. Luncheon was served at the club house, and dinner in the evening was had at the Collier Hotel. The arrangements were made principally by Mr. Edward Morgan, and he and his committee deserve a great deal of praise for the perfection of their arrangements.

As there were twenty-eight prizes to be distributed to those worthies just in from the golf course, Chairman Hempel took his stand among this fine array of prizes, and it was noted that there was intense interest displayed while the names of the winners were read off. The first low net prize went to Mr. G. R. Kremers and the first low gross prize went to Mr. John W. Eich. The weather was good, meals were excellent, the beer was cold, and so a perfect day was enjoyed by all.

Respectfully submitted, ELMER F. SMITH, *Secretary.*

SNAPPED AT N. N. E. OUTING

(See last issue for report)



Proceedings of the American Association of Textile Chemists and Colorists

Dry Carbonizing*

By WILLIAM F. BRANDY and F. E. BURNHAM

Part I—By W. F. Brandy

DRY Carbonizing is done with hydrochloric acid. The acid is volatilized by dropping into a retort at 1000° F. and then entered into the chamber of the machine in which the stock has previously been placed. This is brought about by having a coke fire directly under the retort, and allowing the acid to flow through a ¼" pipe into this retort. This volatilizing of the acid is almost instantaneous, forming what we term Hydrochloric Acid gas. Hence the name dry carbonizing.

Before the gas is introduced into the machine the stock should be thoroughly dried. This is an important factor in any type of carbonizing; in fact no method of carbonizing can be successful unless the material to be carbonized is in perfectly dry condition.

The density of the hydrochloric acid gas is directly and indirectly related to the weight to be carbonized. By this I mean, the density of gas in the chamber has to be as great to do 100 lbs. as it would to do 1,000 lbs. of stock that contains 5% of vegetable matter. But if the stock contains 15 to 20% of vegetable matter the density of gas will have to be increased to compensate for the increased amount of cellulose material to be carbonized.

Mr. Frank Burnham will present a paper later giving more specific data on the chemical points of this process.

Its advantages are:—

1st: The fibers are left in a softer and stronger condition due to the fact that the process is carried on at low temperature, from 150° to 200° F.

2nd: The exposure to the gas is not over ¾ of an hour from start to finish.

3rd: The carbonized cellulose materials do not turn black causing carbon black as in sulfuric acid, hence cleaner stock, more easily washed afterward.

4th: Low cost of operating, not more than 60% of the cost of sulfuric acid; but replacement of parts corroded by the Muriatic Acid brings the total cost up to about the same as for Sulfuric.

5th: Hardly any noticeable change in the color of materials carbonized.

6th: No chance for skips—you either carbonize 100% or you don't carbonize at all.

We have found over a period of 5 years that the quality of this stock is from 25 to 50% better and we would prefer it even at a greater cost.

At this time I wish to extend an invitation to any of the members of this organization who are interested, to come and visit our plant; and I will be most pleased to show our machine and samples of the work it has done. After Mr. Burnham has presented his paper, I will be most pleased to answer any questions you may want to ask.

Part II—By F. E. Burnham

The active agent in dry carbonizing is Hydrochloric Acid, which is a colorless, transparent gas, having an extremely great attraction for water, so much so that it condenses water from the air and also from cotton or vegetable fibres with which it comes in contact.

Hydrochloric Acid is a much stronger acid than sulfuric acid, the usual carbonizing acid. Its pH. is 1 while that of sulfuric is 1.2, and its relative Avidity is 100:49 making it about twice as strong as sulfuric acid. Its degree of Ionization is much greater than that of sulfuric acid and it is much more completely dissociated in solution.

In practically all systems of gas carbonizing, Schirp's, Fitton's, Rothers and Sirtain, etc., a flash evaporation is used, that is:—hydrochloric acid is dropped into a hot retort and the liquid is vaporized and drawn along into the carbzonizing chamber and the composition of the gas in the carbonizing chamber will be the same as the liquid before it evaporated, that is, a mixture of hydrochloric acid gas and of water vapor, as no hydrates of hydrochloric acid could occur except in the liquid phase.

Wool is amphoteric and may absorb and hold hydrochloric acid in three ways:—

1st: Chemically combined, the acid being bound by primary valance forces at the free amino and imino groups and at the peptide linkages.

2nd: It may be absorbed at miscellar interfaces and held by secondary valence forces.

3rd: It may be absorbed in capillary spaces in the wool fiber.

It is also assumed that moisture may be taken up by wool in the same three ways, but not as tenaciously held

*Presented before the May 2nd meeting of the Northern New England Section.

and driven off quickly, so that cotton and cellulose materail is rapidly converted to hydro-cellulose and destroyed.

Dry carbonizing is a simple, fool proof process and would solve most, if not all the difficulties in piece goods carbonizing, and eliminate guess work. It would work equally well in the grease or on scoured pieces, before or after dyeing as colors are practically unaffected and the quality is far superior, due to gentle action and low temperature of the process.

It might be possible to carbonize silk by adjusting the process.

Discussion

Question: How are rags neutralized after dry carbonizing, with water or alkali?

Mr. Brandy: The best neutralizing agent after muriatic acid carbonizing, we will speak of it in that term now, is soda ash. Ammonia works too actively and using it alone, you find that you leave quite a bit of free muriatic acid. Use at least 1/3 the amount of soda ash that you did of acid by weight in carbonizing, to be sure of neutralization.

Question: Couldn't you wash it out with water if you wash it long enough without using any alkali?

Mr. Brandy: Yes, you could.

Mr. Christison: Do you destroy more picker teeth?

Mr. Brandy: The stock is probably neutral, it has no effect on metal.

Mr. Grady: I'd like to ask if the tendency to keep the blue on the original color of the stock applies to most all the blues that you handle or only to serge clips.

Mr. Brandy: Well, we have had to go into that rather deeply so we wouldn't be fooled when we sold the stock saying it was reasonably fast to fulling. You don't know whether they have been dyed with a mordant dye or a union color. We have made tests using the very same types and found that the carbonizing did not change any color at all with the dry carbonizing. With the wet, 40 or 50% came out brown or other colors. Wet carbonizing will take out any union dye such as is put on by garment dyers. If it is men's wear worsted and was originally dyed a blue it will never change.

Mr. Grady: Would it be true of sweater clips?

Mr. Brandy: They change somewhat in dry carbonizing.

Mr. Grady: Don't the acid colors change at all? It is not more noticeably true than the aluminum chloride carbonizing?

Mr. Brandy: Yes. They change some, more than in this dry carbonizing process.

Prof. Olney: How much does this process differ from the one where you treat common salt with sulfuric in a retort located beside the machine and have the hydrochloric acid come over as a gas into the carbonizing drum.

Mr. Wilson: I think it is the same thing except you find that in contrast to the muriatic acid you get an anhydrous gas. The actual carbonizing is the same. It requires apparatus similar to that with muriatic acid except in the steps of generation of gas. Of course, you have a diffent amount of condensation. You have no water.

Mr. Nutting: Is it an advantage or a disadvantage to have the water eliminated as far as the carbonizing process itself goes?

Mr. Brandy: It is an advantage.

Mr. Claflin: Have you ever used anhydrous hydrochloric acid gas?

Mr. Wilson: No. I guess the reason is because it has been hard to get except making it from salt and sulfuric It isn't so difficult to make but cylinder complications make it prohibitive. There isn't any available but it isn't hard to produce.

Mr. Claflin: What is the lining of the carbonizing chamber?

Mr. Brandy: The cylinder in which you put the stock is only cast iron, but the chamber is brick, 16 inch brick walls painted with egg shell enamel. It has been going five years with only slight corrosion.

Question: Have you ever tried the Allegheny metal?

Mr. Brandy: I don't know of it. Of course, it would be more expensive.

Mr. Nutting: Mr. Chairman, in fairness to Mr. Hedenburg and the rest of us too, I think that we might announce that Mr. Hedenburg is here at our invitation because we though that he would be interested, looking at it from a little different point of view from what our friends Mr. Brandy and Mr. Burnham have done. Mr. Hedenburg has had more experience in the application of this process to raw wool, new wool rather than the older re-worked material that our friend Bill has talked about here, and it is in that connection that we invited Mr. Hedenburg to come. I think you will appreciate the fact that he sees it from the mechanical man's viewpoint rather than the chemist's. However, we are interested in knowing about any new developments. There are some details about which he will have to use his own judgment in divulging information, because they are at present in the hands of the patent office, but I am sure he will tell us all that he possibly can and I would like to have him tell us what he can in regard to the handling of raw stock.

Mr. Hedenburg: I came here to hear something myself rather than to talk. We had one of the first rag carboning machines in this country dating back to '86 and were interested even then in applying dry carbonizing to white wool. At that time, Mr. H. D. Gordon read in British Textile Mercury Year Book, that 95% of the rags were

carbonized by the dry process for the reasons Mr. Grady has so plainly pointed out to-night. Then, we started investigating to find out what had been done with virgin raw wool, virgin white wool, in this connection, and we were able to secure very little information. We wrote to nearly all the textile papers in this country and many foreign publications. We took it up with the Department of Commerce and then we built some experimental apparatus. Finally, about two years ago, we worked out a unit which seems to have some promise of success and there seem to be some advantages which we feel make the process perhaps superior to the wet carbonizing methods. We would sum up these advantages as follows:

First: There is usually less shrinkage with the Gas Way method. This result is obtained because we have no wet bowls in which the wool can be lost.

Second: The fibers are not interfered with and the wool is as "lofty" as before processing. The strength of the staple is not impared in the least.

Third: Due to the low temperature used, the color and handle are not changed. These facts were commented on by Dr. Alfred F. Barker, M. Sc. Professor of Textile Industries, University of Leeds, England, who wrote: "It is probable that the softness is retained by baking at a lower temperature than is usual with the "wet" process of carbonizing."

Fourth: The spin and strength of the yarn is not impared by gas carbonization. Therefore, the finished cloth has a breaking strength equal to uncarbonized wool from the same lot.

Fifth: The color of the dyed fabrics are bright and uniform and has a better handle than corresponding fabrics containing wool carbonized by other processes.

I will be very glad to answer any questions in regard to our process. I could talk for an hour or ten minutes on a subject like this and I would be glad to answer any questions.

Prof. Olney: Has any one attempted to carbonize piece goods, that is cloth, with dry hydrochloric acid?

Mr. Hedenburg: Not that I know of. We have had inquiries in that connection and we have made some experiments. To my mind there is no reason why it could not be done. It is merely a mechanical problem.

Mr. Putnam: Mr. Dalton has had a piece done. Perhaps he could tell us something about it.

Mr. Dalton: The process is very efficient in removing burrs, etc. and we are planning additional experiments to run cloth in the machine. It may require shorter lengths of time, more like the ordinary cloth carbonizing machine.

Mr. Grady: I wonder if Mr. Brandy can give us some idea of the rotating of the cylinder.

Mr. Brandy: Yes. The size of the chamber is 10 ft. each way and 14 deep. The cylinder in itself holds 1200 pounds of raw stock revolving two revolutions per minute. We have a fire box built in and connected to the drum with a hole on the shaft. As it heats, the vaporized muriatic acid goes through the hollow shaft into the chamber. As it carbonizes, the revolving of the cylinder dusts the carbon dust out itself, and it drops into the bin below. We never have had a fire with that machine. That is because a low temperature is used. The hole in the shaft is lined with something like an Akron pipe. The only part the acid affects is the retort where you have a hot fire under it, and when the man opens the door the change of air currents sometimes causes a crack.

Mr. Grady: After you saturate that stock with gas, you shut off the gas and do you bake after that at all?

Mr. Brandy: No. While it is in there it does the carbonizing without baking.

Mr. Grady: At what temperature?

Mr. Brandy: 150° F.

Question: After it is neutralized, you dye it in the ordinary way?

Mr. Brandy: Yes.

Question: Does the heat come from the hot gas or from a heating pipe inside the chamber?

Mr. Brandy: We have a heating coil in the chamber and we blow the air through this coil for drying. We stop the pipe when we start gassing. We close the dampers and make the machine as near seal tight as we can so the gas won't leak out. The only heat you get is the heat from the vaporized muriatic that flows from the retort through the hollow shaft into the chamber.

Mr. Claflin: You heat the chamber and then blow the gas in after?

Mr. Brandy: Yes.

Prof. Olney: The cylinder isn't jacketed at all is it?

Mr. Brandy: No. It is a perforated cylinder.

Question: How long does the process take to load and unload?

Mr. Brandy: Four hours for everything.

Question: How much acid is required for 1000 lbs. of stock?

Mr. Brandy: Eighty pounds for the average cotton content of say 20%.

Mr. Clafin: If you want to run it up to 220° F. to carbonize burrs, etc., you could do it but it would break the retort wouldn't it?

Mr. Brandy: I'd carbonize the cotton first and do it over again and carbonize the rest separately. The difference is in the strength of the gas you enter on your stock. You begin to tender your stock after you get to 150. What I would do is to blow it dry again and repeat the carbonizing. You see in our particular line, you have the question of penetration. You have sewing threads that may be through two or three thicknesses of the garment.

Sometimes we use as high as 12% to 14% on the rags while in the wet process you would use 6% to 8% on the raw wool.

Question: I'd like to ask if you have ever used any heating inside the chamber in this process Mr. Hedenberg.

Mr. Hedenberg: Yes. We have used steam coils inside to maintain the temperature. The temperature in the dry carbonizing below 150° F. is a distinct advantage because the wool is not given that harsh feel that you get with the other processes. But, the heating is done inside the chamber.

Question: Does it have any extensive corrosion? Do you use the 100% muriatic gas?

Mr. Hedenberg: We have very little corrosion. We use hydrochloric acid gas. You get almost anhydrous gas. It is a very simple gas to manufacture. The fact that the wool is carbonized at that lower temperature gives you a soft feel and a better condition and also helps out in the dyeing. We have had this experience with wool carbonized by our method. It takes the same shades of dyestuff as the original uncarbonized wool. I have some samples here showing some top dyed with the original wool in delicate shades, and the shades are identical under the same dyeing treatment, which is different from what you get in most carbonized wool.

Mr. Wilson: When you use a dry gas, do you have any trouble with condensation?

Mr. Hedenberg: One of our first experimental experiences was with the muriatic gas condensation. One of our workmen called it condemnation. But this does not occur in our process if you use the salt and sulfuric generator.

Mr. Claflin: Has any one devised a continuous process?

Mr. Hedenberg: When J. P. Devin was alive, we worked with him planning our apparatus and we worked out a continuous process on paper but we have not gone any further with it. We have been so busy working out the details of our process that we haven't reached that point, but I think it is possible.

Mr. Claflin: Has anybody ever tried to make hydrochloric acid by burning hydrogen and chlorine?

Mr. Hedenberg: I don't know of any, but you would have to do that at the plant.

Mr. Claflin: You could have a couple of cylinders. It is very easy to burn hydrogen and chlorine.

Mr. Putnam: Have you made any tests on carbonized colored wool before and after dyeing to see whether there is any effect of chloride in breaking up the chrome molecules?

Mr. Hedenberg: Yes. We have, in our experimenting, tried that and it seems to vary with the type of dyestuff or color. In some cases, there is no change and some cases there is. I presume that if you trace back it is the type of dye used, but I really don't know a great deal about it. In some cases it did turn the shade.

Mr. Putnam: I meant how much effect carbonizing action would have on the chrome lake. I wanted to know if the color was as fast as the original was before the dye had been carbonized. Often the color lake changes though the color itself is not changed at all.

Mr. Hedenberg: I am not enough of a chemist to answer that.

Question: I would like to ask if in the method of generating the hydrochloric acid, there is any chlorine given off? Is it possible for chlorine to be formed which would possible affect the wool?

Mr. Hedenberg: Well, I'll say this. The principal secret of the process if there is any secret is in the preparation of the gas. When we first tried white wool in dry carbonizing, it came out a beautiful brown and there was a reason for it. Our problem has been to remove the cause of that and so our work has been largely with the gas. To-day, with our Gas-Way Process, the wool comes out white.

Mr. Ryberg: You spoke about the dry was method not affecting the dyeing properties. When you used it on white wool, were those samples dyed together or separately?

Mr. Hedenberg: They were dyed together in the same bath.

Mr. Houghton: I have dyed some of the material and it does dye the same shade after gas carbonizing.

Question: How do you get the wool or rags out of the chamber after it is carbonized?

Mr. Hedenberg: The methods are quite different. In the case of wool, we use a fan and gradually extend the extension pipe and suck it out quickly.

Mr. Putnam: I'd like to ask one more question. In connection with the dyeing properties, has Mr. Hedenberg or Mr. Houghton found any condition where you get a resist effect equivalent to what occurs accidently sometimes with sulfuric acid.

Mr. Houghton: My experience has been with laboratory dyeings and there was no evidence of any resist in the samples used.

Mr. Brandy: It would resist in the presence of copper in the stock.

Mr. Christison: Is there any limit to the size of the burrs that are carbonized? We have seen burrs that are large and very dense that are very difficult to remove with the use of sulfuric acid because they are non-absorbent. What becomes of those large hard burrs?

Mr. Hedenberg: We have attacked the problem directly by carbonizing the wool and submitting it to the gas dry so that in the case of the large burrs which retain some

(Continued on page (228) 416)

Proceedings of the American Association of Textile Chemists and Colorists

Degumming of Silk Hosiery*

By VIRGIL T. HARTQUIST
of Wayne Knitting Mills, Ft. Wayne, Ind.

EVEN a resume of hosiery dyeing would be too sketchy to prove of much interest even to you gentlemen not interested in that phase of dyeing, so I have selected the first operation in the finishing of silk hosiery, the boil off or degumming bath and in that operation to dwell chiefly on the most important single factor—Alkali. This, gentlemen, I shall develop from a practical angle.

The total amount of alkalinity is supplied by four principal sources. The soap or boil off oil, the residual alkalinity in the silk from soaking bath, the use of alkalies for fortifying the soap, and the water. Uniformity of finish in the hosiery is essential in processing and to obtain this end standardization must be used to control each of these sources or to determine the amount necessary of one controllable source such as soap to replace a deficiency of another as the soaking residues.

The hydroyl ion derived from the hyrolysis of the soap is the major supply used in removing the silk gum and in its choice particular care should be exercised. Considerable research has been undertaken by soap manufacturers to arrive at the ideal soap for this purpose—Low hydrolysis for the protection of the fibre; good rinsibility; stability against oxidation and rancidity; and stability in the degumming bath from the angle of holding unsaponifiable oils and dirt in suspension are considered the essentials which the soap must possess. Soaps made from high quality olive foots possess these attributes and have found greater popularity in hosiery degumming than any other type. High titre soaps hydrolyze very rapidly in water and have poor rinsibility. Very low titre soaps have as a rule poor stability in the presence of unsaponifiable oils and because of extremely low hydrolysis fail to supply sufficient OH ions to raise the pH to the point of degumming. The iodine value of determination of unsaturated groups which would render the soap unstable and subject to rancidity is very high in these very low titre soaps.

Considerable work has been accomplished on the pH of the degumming bath in relation to that supplied by the soap or oil. Most of this has been in the field of skein or piece goods but can be applied to hosiery. Sericin may be removed in an acid bath of a pH approximately 2.5 or by the proteolytic action of various enzymes, but progress has not reached the point as yet to be of practical value to the silk hosiery industry, so our range of pH must be confined to the alkaline side. Between pH 7 and 8.6, very little sericin is solubilized. Above 8.6 the gum is removed at sufficient rate to permit completion within an hour. Above 10.5 the fibroin is attacked as it is chemically very similar to sericin causing embrittlement and scouring which is the formation of fine ruptured filaments possessing a decreased affinity for dyestuffs. Probably 9.5 is the most efficient pH from the standpoint of fairly rapid removal of the gum and preservation of the intrinsic beauty of silk. This pH can be produced by various alkalies or combined alkalies and buffering salts. Many boil off oils are mixtures of this type. The original boil off oil consisted of sulfonated castor oil and sodium silicate. This was indeed an efficient oil from the standpoint of economy because of its high pH, but sodium silicate embrittles silk quite rapidly also producing a thin papery hand to the hosiery. The most popular boil off oil at present is of a potash red oil base which is partly sulfonated and then saponified, some free oil left in the mixture for lubrication and potassium carbonate used to fortify. To this sometimes is added an organic solvent for solubilizing unsaponifiable oils. The claim for this product is better rinsibility, no resist spots, more levelness on the cotton in one bath method, and better stability in hard water.

Soap is the other product more universally used to produce a pH proper for solubilizing silk gum. A soap made under good control from olive foots will produce a fairly constant pH. This is not dependant upon the concentration of soap. Here we have perfect automatic control from the angle of efficient degumming. The original pH before entering the material is constant because the fatty acid affords the ideal buffering agent which will eliminate sudden shocks of changing alkalies in the water. The hydrolysis reaches a point of equilibrium and if no hosiery is entered into the bath no amount of further boiling will cause further hydrolysis. When degumming begins, the OH ions are used in solubilizing the gum and the equilibrium is unbalanced proceeding as in an equation to the right and freeing an equal amount of alkali as is used by the sericin. Here the total alkali or methyl orange alka-

*Presented at meeting Mid-West Section, May 5.

linity reading must be used instead of pH alone. Various concentrations of soap will give approximately the same pH value but will produce a total alkalinity in direct ratio to the amount of soap in the solution. The pH drops as the sericin combines with the OH ions and if insufficient soap has been used will fall below the pH 8.6 where degumming practically ceases. The amount of soap necessary must be influenced by the other three alkalies.

The second source of alkalinity, the residues from the soaking bath, are of considerable interest in the important effect they produce on the quantities of soap necessary. In recent years, the throwsters of hosiery yarns have through their laboratories developed methods of soaking which will deliver to the mills silk requiring no backwinding over wetting out agents and very little or no conditioning before knitting. The pH of the soaking bath has been raised. Formerly the pH was around 8.3 but has been raised to as close as possible to that point where the gum will be solubilized. I think 9.3 has been found very good pH for this type of soaking. A pH of 10 will cause the gum to strip from the silk when knitting. This soft soaking may be degummed with as little as 5% neutral olive soap on the weight of the goods, the volume being a ratio of 25 to 1, in a four thread number where formerly in harder soaking 15% was required using sometimes an alkaline salt for fortification.

Alkalies fed into the degumming bath for the purpose of furnishing an extra supply of OH are the third important source of alkalinity. They consist mostly of sodium or strongly basic salts of weak acids hydrolyzing to provide their alkali. Chief among these are soda ash, borax sodium, phosphate sodium silicate and sodium sesquicarbonate.

Soda ash has a pH of approximately 11 in a 1/10 N solution. This salt is used considerably but produces a dry sandy harsh handle.

Borax is a very good alkali. It has a pH of approximately 9.5 and is useful when a salt low in alkalinity is needed as in addition to a low temperature degumming in the presence of acilate rayon.

Sodium phosphate has a pH of 11.5 and must be handled carefully because of its strength.

Sodium silicate can easily be the cause of embrittlement but many dyers swear by it.

The sesquicarbonate of soda is a synthetically made salt having a perfect combination. It is a complex molecule containing a molecule of sodium carbonate, 1 of sodium bicarbonate and 2 of water. This assures uniformity of strength and the bicarbonate buffers the carbonate.

Caustic soda will produce excellent result but must be used with perfect control, because very small amounts are needed. Usually this is not practical for dyehouse purposes.

As a rule, these salts are not necessary in the degumming bath but with an unusually hard lot of silk they will be found very beneficial.

Water supplies the fourth effect upon the degumming. I won't dwell on the point long, or I am liable to forget about degumming altogether and find myself talking water, water, and more water. We draw from a deep limestone well with a hardness of 36 grains, 20 of which are calcium bicarbonate. This is far from ideal textile water, especially in the processing of silk. The alkalinity in a water is usually found in the bicarbonate form and as such shall be considered. Upon boiling the half bound carbon dioxide is released and forming the mono-carbonate, the pH rises accordingly. In a water of 350 p p m methyl orange alkilinity, the pH will rise to approximately 10.2-10.6. This is the reaction upon boiling the water without the addition of soap. When soap is added to the water, a reverse reaction seems to occur. Tests I have made in distilled water in comparison with the well water show a higher pH by about .5 of a pH. This phenomenon occurs also in laundry scouring. Laundry formulas based on eastern waters of low alkalinity prove of insufficient strength when used in midwestern waters. A solution of soda ash or suitable alkali must be added for a kick or more soap is necessary. This alkalinity which is supplied then by the water in the degumming bath, because of its lower pH 2 (Bicarbonate having a pH of 8.3) depresses the pH of the degumming bath.

There we have the four principal supplies to be controlled. For control there must be for uniformity of finish. Degumming may be used for a variety of handle in hosiery. Clean complete removal of the gum produces a clean scroopy feel. Approximately ½% will leave the silk in soft somewhat lifeless handle. 2% to 3% gives to the stocking a wiry stiff condition which is sometimes used for chiffons. Each sales department has its own idea about hosiery from this angle, and the dyer has these tools to control his finish from the angle of degumming.

DRY CARBONIZING

(Continued from page (226) 414)

moisture, the bigger they are the better they carbonize because the large burrs absorb more gas and are more easily destroyed than the smaller burrs.

Mr. Wilson: The dryer the gas is, the more efficient the carbonizing is. Is that so?

Mr. Hedenberg: No. That doesn't necessarily follow.

Mr. Nutting: Mr. Brandy brought out the point that copper had an influence on the resistance of the wool. I wonder if there are any other metals that would influence it that way.

Mr. Brandy: None that I know of. We have found that copper is the only thing that worked out that way.

AMERICAN
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VALUE OF AN OUTING

DURING the months of June and July many of the various trade associations hold what they term "outings" and in many cases these outings have become time honored institutions. Just why have these outings continued year after year and why do they continue to be the biggest drawing card of the entire season? Primarily they serve to give those in attendance a good time and as we all enjoy a good time it is easy to see why this fact alone should attract a large attendance. But there must also be other reasons why we are attracted as surely we all have good times without attending outings. Our own good times however are with *personal* friends and at the outings we enjoy ourselves with our *business* friends. True, in many cases, our business friends are also our personal friends but in the cases where we are acquainted only through business connections it gives us an opportunity to meet these friends on an entirely different basis than we do in our ordinary business life and in many cases business acquaintances become personal friends. This then is probably the primary reason why we are drawn to the outings—to develop our business acquaintances through the medium of a good time. You may know a person through business connections for years and always address him as "Mr." and after one outing it may become "Jim" or "Jack" and so on.

Another reason why we may be attracted to these outings is because it gives us a day off from business and who doesn't appreciate a holiday in the midst of a business week? A day off is always an attraction but generally we must have an excuse for taking it. The outing furnishes us this excuse and we are willing to take advantage of it. But we would not be willing to take advantage of it if we did not get something out of it, either in the form of pleasure or in some other form. However we think this reason is the smallest of any for attending the outings although it probably contributes to the attendance in its own way.

We must also consider why the various associations are willing to sponsor these outings. By this we mean that the organizations must think they are worthwhile to put in the amount of work and money that is necessary to properly stage such an affair. Perhaps the reason is that most of the outings are used to close the season of the associations after the usual business of technical meetings during the year from the past fall until the summer and it provides a sort of gala wind-up. It draws out more of a crowd than any of the usual meetings and disseminates a spirit of cordiality that will tend to draw the members back to the meetings when they start again in the Fall. It provides a common meeting ground for those who are perhaps too seriously disposed ordinarily and those who are too playfully minded. It draws the former perhaps because of loyalty to the association and the latter because of a natural interest in a good time. But this we do not mean that the former attend only because they think they ought to but rather because it gives them an excuse in their own minds for having a good time. Whatever the reason it draws the crowd and provides a good ending for the season. A good ending will do more to start the next season off right than anything else as it lingers longer in the minds of those who attend the usual meetings rather spasmodically. It reminds us of the old fashioned Sunday School picnics when we would attend Sunday School regularly so that we would be among those present at the time of the picnic. It did not seem so hard to return to Sunday School later on. The picnic acted to keep our interest alive and perhaps it is in the same manner that the outings serve to keep alive an interest in the trade association. Many who do not attend any of the meetings during the year are present at the final outing and it thus keeps alive a spark of contact that otherwise might die out altogether.

We do not mean to intimate that the associations are not strong enough to survive without an outing to revive interest for such an association would be weak indeed and with but little excuse for existing. We do think however that the outing has a proper place in the program of the various trade and technical associations in the textile field and that it is really worthwhile for those who do attend. Many of us perhaps lose interest in the activities of our associations through various reasons and as the outing serves to draw us back again it does serve a useful purpose.

DYE ABSORPTION OF COTTON FIBERS

(Continued from page 395)

be composed of the same cellulose as the growth rings, but does contain fatty matters. Results show that there is little of the coloring or spotting which usually indicates the presence of substances other than the usual cellulose, and that mordant and ingrain dyes, which seemed to present more evidence of adsorption than absorption, only form fine colored spots on the outer surface. It would seem from a chemical point of view that the green fiber is mainly composed of unruptured cuticle, and that it has not developed the normal fatty matter. From a physical viewpoint it would seem that since striations, wall pits, and lumen appear to be partially or wholly absent from green fibers, that there would be less surface exposed for absorption, and no opportunity for a possible adsorption other than on the outer surface.

Under-ripe fibers take dye better than green fibers, but not nearly as well as normal fibers. It would appear that slightly better dyeing is obtained than in the green fibers because there is a lumen in which dye may become adsorbed, and more impurities with which dye might combine. One unusual case was noted where several unbleached tendered fibers dyed a beautiful pink by the acid orange.

The effect of chemical treatment was well illustrated by the normal fibers, and corresponded with the findings of previous investigators. In all types of fibers the unbleached showed more spottiness than the bleached, which was to be expected. Oxidation showed a heavy increase in dyeing; mercerization gave the expected results; tendering caused the expected heavy dyeing by the basic dye. As in the case of the under-ripe fiber, most of the dye appeared to be in the lumens.

All of the over-ripe fibers showed an abnormally heavy dyeing, with the exception of the case of the basic dye on the mercerized samples. There is perhaps sufficient chemical evidence to explain this. Most of the dyes, particularly those which used mordants or any other reagents which might precipitate in the fiber, gave a darker shade than was intended. The dye was precipitated throughout the fiber and particularly in the lumen, in the form of spots, streaks, splotches, and smears. The acid dye, which had little effect on the other classes of fibers, caused a heavy darkening of the over-ripe fibers, and seemed to mark particularly the lumen. There is perhaps some decomposition of cellulose in this type of fiber, as well as a possibly unusual content of the various substances usually classed as impurities, and which are normally removed by kier boiling or solvent extraction. The presence of these substances would explain unusual chemical activity toward dyestuffs. Results indicate that the various chemical treatments tend to increase the ability of these fibers to absorb dye materials or lakes, and it may be concluded that over-ripe fibers possess a much greater porosity and more accessible lumen than normal fibers. Hence it

TABLE II—THE EFFECT OF DYES ON COTTON FIBERS

Dye	*Green*	*Under-Ripe*	*Normal*	*Over-Ripe*	*Dead*
DIRECT Congo Red	B: Pale to colorless. U: Pale to colorless. M: Very pale BO: Pale to colorless UO: Very pale BT: Pale UT: Pale	B: Pale red U: Red. Spotty M: Slightly pale BO: Pale UO: Deep black Lumen and spotted BT: Pale UT: Good color. Very few spots	B: Red. Deep red spots in L U: Red. Spotty M: Full red BO: Reed red. Dark streaks UO: Deep. Black L. Spotted BT: Even color. Few spots UT: Good color. Few spots	B: Deep red. Very spotty U: Deep red. Badly spotted M: Blackish red BO: Dark red. Black streaks UO: Deep. Spotty. Almost black BT: Even color. Few spots UT: Deep. Badly spotted. L. black	B: Pale U: Very pale M: Muddy red BO: Very pale UO: Very pale BT: Very pale UT: Pale

BASIC Malachite Green with Tannic Acid	B: Very pale U: Very pale M: Very pale BO: No color. Few spots UO: Almost colorless BT: Almost colorless UT: Almost colorless	B: Pale. Color in lumen U: Very pale M: Very pale BO: Pale. Few spots UO: Good color BT: Pale muddy green UT: Light muddy green	B: Dark green U: Dark green. Ppt in Lumen M: Pale BO: Pale. Spotty; dark green UO: Good color BT: Deep. Badly spotted UT: Deep. Badly spotted	B: Deep green U: Deep. Spotty. Heavy Ppt in. M: Pale BO: Dark. Heavily spotted UO: Black with color BT: Deep. Badly spotted. Streaks in Lumen UT: Almost black. Smeary	B: Deep green U: Deep green M: Very pale BO: Blackish color UO: Dirty color BT: Colorless. Few spots UT: Almost colorless. Few green spots
ACID Acid Orange II with Acetic Acid	B: Very pale U: Almost colorless M: Colorless BO: Almost colorless UO: Very pale pink BT: Colorless UT: Almost colorless	B: Very pale. Few streaks in L. U: Pale pink M: Almost colorless BO: Almost colorless UO: Pale pink, few spots BT: Almost colorless. Few spots UT: Few with good color	B: Very pale. Dark Lum. U: Pale pink. Black spots in L. M: Pale. Streaky Lumen BO: Almost colorless. Spotty L. UO: Pale. Heavily spotted L. BT: Almost colorless. Few spots UT: Few with good color	B: Heavily marked. Dark L. U: Black spotted all over M: Dark colored. Spotty BO: Badly spotted. Smeary UO: Dark. Heavily spotted BT: Almost colorless. Few spots UT: Blackish spots	B: Colorless U: Almost colorless M: Colorless BO: Colorless UO: Almost colorless BT: Colorless UT: Colorless
MORDANT Alizarin with Feric Acetate	B: Very small spots U: Very small spots M: Few small spots BO: Faint spotty brown UO: Faint spotty brown BT: Faint spotty brown UT: Faint spotty brown	B: Spotty brown U: Spotty brown M: Slightly colored BO: Light spotty brown UO: Light spotty brown BT: Light spotty brown UT: Light spotty brown	B: Spotty brown. Few streaks L U: Spotty brown. Spotty L. M: Medium brown. Spotty BO: Deep spotty brown in L. UO: Deep spotty brown in L. BT: Light. Dark spotted L. UT: Light. Dark spotted L.	B: Splotchy dark brown U: Splotchy, muddy dark brown M: Splotchy brown BO: Blackish brown in L. UO: Deep splotchy brown in L. BT: Deep splotchy brown UT: Deep splotchy brown	B: Spotty brown U: Large brown spots M: Spotty brown BO: Spotty brown UO: Spotty brown BT: Faint spotty brown UT: Faint spotty brown
VAT Indigo $FeSO_4CaO$	B: Very pale U: Colorless M: Colorless BO: Very pale UO: Very pale, slightly spotty BT: Very pale to colorless UT: Almost colorless	B: Very pale. Few spots in L U: Very pale, spotty M: Very pale BO: Very pale, blue in L UO: Pale spotty blue BT: Almost colorless UT: Almost colorless. Few spots	B: Deep color. Mostly in L. U: Deep in Lumen. Spotty M: Faint blue BO: Good color. Spotty L. UO: Spotty blue in L. BT: Faint. blue and black in L. UT: Faint spotty blue	B: Heavily colored in L. U: Heavily colored in L. Spotty. M: Deep blue BO: Heavily colored in L. UO: Deep blackish blue. Spotty BT: Heavy blue and black in L. UT: Deep spotty blue and black	B: Colorless U: Colorless M: Colorless BO: Few pretty blue UO: Almost colorless. Spotty BT: Almost colorless. Spotty UT: Almost colorless
INGRAIN Anilin Black	B: Pale. Not smooth U: Pale. Not smooth M: Pale. Not smooth BO: Pale, spotty UO: Pale. Not smooth BT: Very pale. Not smooth UT: Pale. Not smooth	B: Pale. Not smooth U: Pale. Spotty M: Pale. Few spots BO: Pale. Heavy spots UO: Pale. Not smooth. Streaky L BT: Very pale. Few streaks in L UT: Pale. Streaky L. Few spots	B: Pale. Streaky L. Not smooth U: Black. Spotty Lumen M: Black. Streaky Lumen BO: Black. Heavily spotted L. UO: Black. Heavily spotted L. BT: Pale. Few streaks UT: Pale. Few streaks	B: Pale. Heavy black splotches U: Heavily spotted black M: Heavy spotty black BO: Deep. Badly splotched UO: Deep. Splotchy Lum. BT: Pale. Few splotched UT: Heavily splotched L.	B: Very pale. Not smooth U: Pale. Heavy spots M: Pale. Heavy spots BO: Pale. Spotty UO: Pale BT: Very pale UT: Very pale

B: Bleached; U: Unbleached; M: Mercerized; BO: Bleached Oxidized; UO: Unbleached Oxidized; BT: Bleached Tendered; UT: Unbleached Tendered.

might be said that over-ripe fibers are more receptive toward dyes than normal fibers because of both physical and chemical differences.

Dead fibers seem to be physically and chemically different from green fibers; yet they gave almost the same results. One surprising result was the dyeing of bleached, unbleached, and oxidized fibers by the basic dye. This heavy dyeing indicates a chemical nature receptive to basic dye, but the action of tendering did not increase dyeing. Haller[17] reported that dead fibers would take more dye than normal fibers, but this classification included fibers which are herein classified as over-ripe. It was found that dead fibers absorbed no more dye than green fibers, except after having been mercerized. These samples were a muddy color.

Conclusions

1—That growth condition determines the dyeing properties of cotton fibers.

2—That differences in the dyeing properties of the various types are due to both physical and chemical differences in the fibers.

3—That cotton gathered under conditions most favorable to produce normal fibers gives the best results when dyed.

[17]Loc. cit.

Textile Foundation News

Improving the Quality of Raw Cotton

RECOGNIZING that obtaining a higher quality of raw material is an important way of aiding the cotton producer and the textile industry, the Textile Foundation recently has ear-marked some of its funds for aiding research on methods of improving the quality of raw cotton.

Decision to go forward with this project was reached after Secretary of Agriculture Wallace and Stuart W. Cramer of Cramerton, N. C., as a sub-committee of the Board of Directors, developed convincing evidence of the value of such practical research. In the course of the preliminary inquiries, Messrs. Wallace and Cramer were fortunate in securing the advice of men of professional and practical experience.

Part of the fund is being used during the current year to help finance comprehensive regional varietal trials of a number of the more or less standard varieties of cotton by the Bureau of Plant Industry of the U. S. Department of Agriculture and the State experiment stations in North Carolina, Tennessee, Arkansas, Oklahoma and Texas.

It is generally recognized by the cotton trade, both in the United States and abroad, that the spinning utility of the great bulk of the cotton now grown in this country is far below what it should be. One of the principal causes of this poor quality is that too many different varieties are grown in the same locality. The result is that the cotton becomes mongrelized through cross-pollination between different varieties and by the mixing of seed from different fields at the gins.

More than 1,200 different names for cotton varieties being grown in the United States have been recorded and about 400 of these have been added in the last 10 years. Only about 5% of the approximately 600,000 tons of seed required to plant the crop comes from seed breeders, the remaining 95% being largely of such mongrelized gin-run stocks. Seed mixing and primitive cultural practices have resulted in millions of dollars needlessly lost every year to the textile industry and to growers, through low yields of short, irregular fiber of poor spinning quality.

The length of staple and quality of the crop can be improved rapidly through a larger use of pure seed of superior existing varieties. Premium varieties do not deteriorate or "run out" if the seed is kept pure. The establishment of communities within which only one variety is grown and ginned aids in providing large supplies of pure seed. Many single-variety communities have been organized during the past several years and the number is increasing as the practical advantages are becoming better recognized. In order to insure the agricultural as well as the textile value of the varieties selected for community planting, it is necessary to have adequate experimental data on the varieties before they are recommended.

The State Experiment stations throughout the Cotton Belt have tested varieties in various localities for many years. The current trials being aided by the Textile Foundation will incidentally provide some supplemental information along this line. Their primary purpose, however, is to supply data on the broader, regional adaptation of varieties, to help delimit the areas where one class of varieties should give way to another, and to supply basic information on the effect of change in environment on different varieties of cotton grown under the same plan. In addition to yield and other agronomic data, the Bureau of Agricultural Economics of the U. S. Department of Agriculture will cooperate in making comprehensive laboratory and experimental mill studies of the fiber from samples of known variety and production history. These should provide a valuable basis for further studies of the roles of inheritance and environment in determining fiber quality.

The Textile Foundation, with headquarters in Washington, D. C., was organized four years ago for scientific and economic research for the benefit and development of the textile industry, its allied branches, and including that of production of raw materials.

OPEN FORUM

Rules under which this department of the REPORTER is conducted are as follows:

1. Anyone who has a technical problem on which he would like advice may submit it to the Reporter and it will be published in the first available issue.

2. Any reader who feels that he has a solution of the problem may forward his reply to us and if we feel that the reply is suitable it will be published in a succeeding issue.

3. For each such reply published the Reporter will pay a minimum of $2.

4. In case there is more than one answer to the same question, the one covering the subject in the most complete and authentic manner will be published, or if two answers are sufficiently different both will be published. If two answers are considered equally good, the one first received will be given priority.

5. The Reporter will assume no responsibility whatsoever for the accuracy of the answers submitted—it is simply offering a vehicle for the public expression of its readers' opinions.

6. Both the questioner and answerer must send in his complete name and address. When requested we will publish only the initials or other identifying insignia.

Answers

9—I am making tallow softeners on a laboratory scale. To what tests can I subject these tallow softeners in order that I ascertain if they will injure the cotton goods, become rancid, or decompose to form an objectionable compound? I am referring to softeners suitable for cotton piece goods only.—**J. E. G.**

Answer—To counteract the rancidity which is apt to develop in tallow softeners, zinc chloride and other zinc salts, or occasionally certain proprietary mould inhibiting agents, are added to the mixture. To determine if sufficient quantity of these preservatives have been employed in a particular mixing, first test an untreated sample of cotton cloth for tensile strength (This requires a "bursting" machine, or similar type testing machine.) Then heavily impregnate a sample of cotton cloth with the softening. Remove the sample away from the light and keep at blood-heat, or just below, under conditions of humidity. This will encourage the formation of ferments, free acids and mildews, etc., where inhibitors have not been employed in the correct proportion. Finally, the sample should be microscopically examined and re-tested for tensile strength.—A. I. C.

10—We have a particularly difficult problem in holding our bleachery on a set shade or white, due partially to the standard getting soiled from handling as well as from yellowing with age.

We would like some information as to how other bleacheries hold their standard shade of white.—**M. P. C.**

Answer—Most bleachworks experience the same difficulties from patterns getting soiled, and in the majority of cases, just renew with a fresh reference pattern. Reference patterns are usually kept of all the different cloths or yarns going through, as the same white can never be obtained on, say, Indian cotton as that obtained on Egyptian cotton.

The following is rather an ingenious way of keeping a standard of white: A standard quantity of barium sulfate is prepared and tinted to the exact hue with ordinary ultramarine. This is kept in corked glass containers and is always perfect.—A. I. C.

12—Please give me a method for dyeing ivory, stating any unusual precautions which it may be necessary to observe.—**B. T.**

Answer—It is not recommended to attempt the coloring of whole tusks of ivory in the absence of necessary machines for forcing the dye liquor throughout the tusk.

Acid dyes are usually applied with about one-half pint acetic acid per 20 gallons of liquor. Dyeing is carried on for about one hour at the boil. In order to secure better penetration, it is better to use the requisite amount of acid in two or three additions.

Basic dyes may be applied similarly to acid colors, but boiling for about half an hour, usually suffices.

Direct dyes are dyed for one hour at the boil, with the addition of about 1 pounds of Glauber's salt and 4 ounces of soap per 20 gallons of liquor. The ratio of ivory to liquor is usually about one part of ivory (by weight, of course) to fifteen parts of water. More soap is required if there are any signs of too speedy absorption of the dyestuff.

It is most essential to see that in all cases the dyestuff is thoroughly dissolved, otherwise splotches easily form on the ivory and these are most difficult to disperse.

After dyeing, the ivory is allowed to dry by packing in hot sawdust, and the pieces are then examined for signs of inequality in color. Any light places may then be touched up with a camel hair brush, charged with a weak solution of dyestuff in alcohol, benzine or other suitable solvent of quick drying properties.

A finish is usually obtained by oiling and polishing. Olive oil is frequently used, but in this event, it is well to add also a small proportion of laurel oil to counteract decomposition and subsequent clouding of the luster.—A. I. C.

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etc. The case cited is most serviceable as a precedent in that it indicates, in the one instance, the scope of the Commission's mandatory power as applied to invasion of preempted color in the case of both the primary product and the packaging and advertising of the product by means of sympathetic color expression.

No less in the sphere of design pioneering than in color concentration and capitalization has the Trade Commission set its face consistently against simulation capable of promoting substitution of goods. Long before the first NRA Code was thought of, the Trade Commission was making design integrity one of the pillars of the average industrial treaty. A standard rule in the set-up of the usual Trade Practice Conference denounces the practice of a manufacturer of usurping or pirating the design developed or produced by a competitor "as an unlawful taking of private property, opposed to the best interests and good name of the industry and is condemned by the industry."

One of the most fruitful efforts of the Federal Trade Commission has been that which has opposed the use of color designating terms in other than an adjective sense. This enforcement of the generic status of color specifications dates back some fourteen years to the time of the Trade Practice Conference of the pyroxylin plastics industry when it was agreed that words such as "ivory" "amber" "jade" and "coral" should be employed for descriptive purpose only when coupled with a qualifying term indicative of color or finish.

Imitation of design, when carried out for the purpose of, or with the effect of "passing off" goods emanating from a source other than the inventor, author, or initial adapter of a design has, from the earliest days of the Trade Commission been deemed a major provocation for issuance of a Cease and Desist Order. Similarly, concert of action within a trade to promote mutual respect for virgin property in design has been an approved objective of the self-regulation ritual since 1928 when the shirting-fabrics industry, under the wing of the Trade Commission, went on record as unalterably opposed to any piracy of styles and pledged effort on the part of manufacturers and converters to put an end to this form of trespass.

In key with the policy of particularization as to color terms, above noted, has been the policy of the Trade Commission in requiring, over a period of years, use of the word "dyed" or equivalent indicia of processing when needful to the understanding, by the lay public, of a trade vocabulary. This supplementary use of dyed is exampled by "black-dyed fox". And, in the case of a country or place used to designate color, by the amended "Sitka-dyed Fox".

A prime inducement for recourse to the Trade Commission for any corrective needed to invoke protection for color rights or design rights is found in the circumstance that the Commission bears the entire expense of any prosecution it may make its own. Furthermore, the identity of the instigator need not be disclosed to the parties whose methods are challenged. It is to be borne in mind however that the jurisdiction of the Trade Commission covers only interstate commerce.

SIZING DEFECTS IN GRAY GOODS

Gray goods manufacturers should be held as responsible for sizing and other materials that are difficult, or impossible, to remove in the finishing processes, as for imperfections of fabric structure, according to an editorial in the July issue of Textile Research, the official organ of U. S. Institute for Textile Research. It is claimed that "Gray goods that contain mineral or vegetable oils, waxes, gums, or other materials that are not readily soluble or emulsifiable in the finisher's regular 'prepare' are not 'satisfactory commercial deliveries.'" U. S. Institute has prepared a bulletin covering "Sizing Ingredients That are Partly or Wholly Insoluble, and Those That are Soluble or Emulsifiable" that may be had by addressing the Secretary at 65 Franklin St., Boston, Mass.

Other articles appearing in the July issue of Textile Research are the following: Effect on the X-ray Pattern of Drying Caustic Pretreated Cotton, by Bancroft, Calkin and Stillwell; The Microbiology of Textile Fibres by Bryce Prindle; X-ray Analysis of Textile Fibres by Wayne A. Sisson; Relation of the Sheep's Health to the Growth Rate of Wool by J. F. Wilson, and the regular abstract section covering scientific textile research throughout the world.

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The rate for "Position Wanted" advertisements in this column is 2 cents a word—with a minimum of 50 cents per insertion. For all other types of advertisements—i.e., help wanted, machinery or supplies for sale—the rate is $5.00 per column inch or less per insertion.

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